A TWO-DIMENSIONAL MODEL OF A SINGLE-CHAMBER SOFC
WITH HYDROCARBON FUELS

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ABSTRACT

A 2D numerical model of a single-chamber fuel cell (SCFC) running on hydrocarbon fuels is presented. The SCFC concept is a novel simplification of a conventional SOFC in which the anode and cathode are both exposed to the same premixed fuel/air mixture, and selective catalysts promote electrochemical oxidation of the fuel at the anode and simultaneous electrochemical oxygen reduction at the cathode. Laboratory tests of small designs of SCFC have demonstrated excellent electrical performances. The model solves for the velocity, temperature, and species distributions, as well as the current density profile, in an SCFC stack for a specified electrical bias. The anode partial oxidation / reforming chemistry use a multi-step elementary reaction mechanism, and electrochemical oxidation of the resulting hydrogen and/or carbon monoxide is included. The set of transport equations in the gas channel is integrated with SIMPLEC algorithm. Simulated trends are in good agreement with experiment.

INTRODUCTION

A single chamber fuel cell (SCFC) is one in which the anode and cathode are both exposed to the same premixed fuel/air stream, and selective electro-catalysts are used to preferentially oxidize the fuel at the anode and reduce oxygen at the cathode. Laboratory tests with small SCFCs have shown that they can produce useful power densities running on hydrocarbon fuels (2, 3). While the efficiency is typically lower than that of conventional dual-chamber SOFCs, SCFCs do not require seals, and allow a very simply gas manifold design. For some applications, notably small-scale power generation, the mechanical simplicity of an SCFC design may make it more attractive than a dual-chamber SOFC, despite the lower efficiency.

Since SCFCs require selective electro-catalysis, they must operate at temperatures low enough that the catalysts maintain some degree of selectivity; this typically limits the temperature to below 700°C, which is significantly lower than that of conventional SOFCs with YSZ electrolyte. And because complications due to sealing are eliminated, the SCFC greatly simplifies the system design and enhances the thermal and mechanical shock resistance, thereby allowing rapid start up and cooling down (1).

In an SCFC, reforming and catalytic partial oxidation of the incoming fuel stream supplies H₂ and CO for electrochemistry. The studies of Hibino (3) and Shao (1) show
that methane, ethane, propane and liquid petroleum gas are all potential fuels for an SCFC. Hibino et al. (8) recently reported achieving a power density of more than 400 mW/cm² at a temperature as low as 500°C using a Ni-CeO₂ cermet anode and a cathode made of Sm₀.₅Sr₀.₅CoO₃. Shao et al. (1) achieved a power density of more than 700 mW/cm² at 650°C using a single-chamber configuration with a Ni-SDC anode, a Ba₀.₅Sr₀.₅Co₀.₈Fe₀.₂O₃ (BSCF) cathode and methane as the fuel. To date, experimental studies have shown that the efficiency is lower than that of an equivalent dual channel cell due to parasitic catalytic combustion and slight drop in Nernst potential because of premixing the fuel and air. However, since the first reports of successful operation of SCFCs are quite recent, the potential of this novel type of fuel cell is not yet known.

Besides the selectivity of the electro-catalysts, there are many other factors that influence SCFC performance. For example, at the atomistic level, the performance of the cell is dictated by the interplay of a variety of physical or chemical processes, including surface chemistry on the anode and cathode, heat transfer, transport of the gaseous reactants and products within the cell, and transport of mobile ions through the solid electrolyte (1). At the mesoscale, the cell performance is dictated by the system fluid mechanics, species transport, and competition between various modes of heat transfer. Optimal design of a SCFC depends on understanding and quantifying all these complex processes, and thus a comprehensive model of at least 2D is needed. Modeling can play a very useful role in interpreting experimental SCFC performance data and in design and optimization studies. In this paper, we present a two-dimensional numerical model of an SCFC running on hydrocarbon fuels.

**SCFC Operation**

Figure 1 shows the operation of a single cell with the stack configuration, which has a thin, dense, solid oxide electrolyte layer sandwiched between two porous electrodes. Partial oxidation over the anode catalyst supplies H₂ and CO for the electrochemical reactions. A fuel rich gas mixture is required to produce CO and H₂ without producing significant amounts of CO₂ and H₂O (1).

The cell in this study is anode-supported. For hydrocarbon fuels, this structure has some advantages in that the electron-carrying metal can also serve as a reforming or catalytic partial oxidation (CPOX) catalyst (5). In such a system the anode is usually on the order of one millimeter thick, while the thickness of the cathode is only a few tens of microns (5).

The electrolyte thickness is typically 10-20 μm to minimize ohmic losses. Although YSZ is the most frequently used electrolyte material for SOFC, it is unlikely to be used at temperatures below 700°C due to significant ohmic loss, and alternative materials such as ceria, lanthanum gallate or proton conducting electrolytes such as barium zirconate are needed (1). In this study, we use ceria as the electrolyte.
The Gas Channel Flow Model

The SCFC model consists of several coupled sub-models. Here the model for the gas flow around the SCFC cell(s) is presented, followed by discussion of other sub-models for the transport and reaction within the cell.

The flow model determines the two-dimensional velocity, density, temperature, and species mass fraction fields in the gas surrounding the cell. It is coupled to a separate model for the transport and reaction processes within the cell (described below) at the gas-cell interfaces. The gas is modeled as an ideal gas mixture of species with homogeneous chemistry neglected. Zhu et al. (9) reported that at temperatures below 800°C and residence time of a few seconds only a few percent of the methane fuel is reacted in homogeneous reactions. Walters et al. (7) have shown that the temperature needs to approach 900°C for gas-phase chemistry to play a substantial role for SOFCs using natural gas as a fuel.

A zero-Mach number, variable-density formulation of the conservation equations is used. For fuel cell applications, the assumption of zero Mach number is a very good one, since typical gas velocities are less than 1 m/s, in order to provide sufficient residence time to complete the electrochemical oxidation process. The density variation results from the spatial variation of the chemical composition (and therefore mean molecular weight), as well as the temperature of the gas, but not from the finite Mach number.

The velocity field is determined from the continuity equation

\[ \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \]  \[1\]

and the momentum equation

\[ \frac{\partial \rho \mathbf{u}}{\partial t} + \nabla \cdot (\rho \mathbf{u} \mathbf{u}) = -\nabla P - \frac{2}{3} \nabla (\mu \nabla \cdot \mathbf{u}) + \nabla \cdot [\mu (\nabla \mathbf{u} + (\nabla \mathbf{u})^T)] \]  \[2\]

with the density determined by the ideal gas equation of state

\[ \rho = \frac{P_0 W}{R T}, \quad R = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \]  \[3\]

The temperature distribution is obtained by solving the energy equation

\[ \frac{\partial \rho T}{\partial t} + \nabla \cdot (\rho \mathbf{u} T) = \frac{1}{c_p} \nabla \cdot (\lambda \nabla T) - \frac{1}{c_p} \sum_{k=1}^{K} \frac{c_{p_k} D_{km}}{\rho} \nabla Y_k \cdot \nabla T \]  \[4\]

The species mass fractions \( Y_k \) \((k = 1, \ldots, K)\) are determined from the species mass conservation equation

\[ \frac{\partial (\rho Y_k)}{\partial t} + \nabla \cdot (\rho \mathbf{u} Y_k + \mathbf{j}_k) = 0 \]  \[5\]
In these equations, $\mu$ is the dynamic viscosity, $D_{km}$ is the mixture-averaged diffusivity of species $k$, and $J_k$ is the modified diffusive mass flux for species $k$ defined by

$$J_k = \dot{J}_k + \dot{J}'_k \tag{6}$$

where

$$\dot{J}_k = -\rho D_{km} \nabla Y_k, \quad \dot{J}'_k = -Y_k \sum_{k=1}^{K} \dot{J}_k \tag{7}$$

such that

$$\sum_{k=1}^{K} \dot{J}_k = 0 \tag{8}$$

Discretization and integration of governing equations [1], [2], [4] and [5] employ the SIMPLEC algorithm (10). The spatial derivatives are discretized using a 2nd-order accurate approximation, and the equations are integrated over a control volume of width $\Delta x$ and height $\Delta y$ using the finite volume approach. A staggered grid is used on the computation domain, with scalars defined at the center and vector components at the faces of a control volume (10). The equations are marched in time until the steady state solution is obtained. The model can simulate SCFC performance with or without solving the energy equation [4]. At this stage of the model development, isothermal simulation usually provides more insights in parameter exploration of the SCFC design.

**The Porous Electrode Transport Model**

In order to determine the composition of the gas at the electrode / electrolyte interface, where the electrochemistry is assumed to take place, it is necessary to compute the coupled problem of transport and reaction within the pore network. Only reactions occurring on surfaces are considered, due both to the low temperature and to the small pore size, comparable to the mean free path for the molecular species.

The porous electrode model is formulated in terms of the gaseous species of the flow model, and in addition a set of adsorbed surface species on the catalyst particle surfaces with which the gaseous species may react. The mean concentrations $\rho_k (k = 1,\ldots,K)$ of the gaseous species in the pores are determined by solving the porous-media gaseous species conservation equation

$$\nabla \cdot \dot{J}_k = A_c W_k \delta_k, k = 1,\ldots,K \tag{9}$$

where $\dot{J}_k$, $W_k$ and $\delta_k$ are respectively the diffusive mass flux, molecular weight and molar production rate on the catalyst surface of species $k$, and $A_c$ is the volumetric specific surface area of the catalyst. The coverage fractions $\theta_k (k = 1,\ldots,K_s)$ of the surface species are computed self-consistently with the gaseous species, by requiring that the surface species are all in steady state, and therefore their net chemical production rates are zero.
\[ \delta_k = 0, \quad k = 1, \ldots, K_s \]  

where \( K \) and \( K_s \) are total number of gaseous and surface species, respectively. \( \delta_k \) is supplied by the heterogeneous chemistry mechanism (for the anode) that will be discussed shortly. The mass flux \( j_k \) depends on the gradient of \( \rho_k \), and is evaluated by the Dusty-Gas Model (DGM) (11). The DGM used in this study accounts for the major mechanisms for gaseous molecular transport in porous media including bulk molecular diffusion, Knudson diffusion and Darcy flow (11, 12). Zhu et al. (9) have discussed the application of this model in SOFC anode in detail.

This model is formulated as a steady-state model, even though the flow model, to which it is coupled, is formulated in time-dependent form. This is advantageous, since the inclusion of fast reactions would otherwise require very small time steps and long computation times. Since only the steady-state solution is of interest, there is no error introduced by this procedure. This allows solving these equations using a fully-implicit algorithm for stiff systems. Given the mass fractions of the gaseous species at the electrode/gas interface, it solves for the steady-state species fluxes through the electrode and surface coverages. The computed fluxes at the electrode/gas interface are fed back to the flow model, where they are incorporated into the discretized species conservation equation as boundary conditions, and the interface velocity \( v = \sum_{k=1}^{K} j_k / \rho \) is used as the boundary condition for the momentum equation [2].

**Heterogeneous Chemistry**

The model is implemented in a manner so that different reaction mechanisms describing the heterogeneous chemistry on the catalyst particle surfaces may be easily used. For the calculations presented here, we use an elementary multi-step reaction mechanism that accounts for the partial oxidation and steam reforming of methane over a nickel surface. The mechanism consists of 46 heterogeneous reactions between 6 gaseous species and 13 adsorbed surface species (13). Although coking is a common problem with Ni in reforming reactors, it can be controlled through careful management of cell operating conditions (6). In particular, in an SCFC, coking is less of a problem due to the presence of oxygen at the anode. In this study, we consider only fuel/air ratios for which coking is not a problem.

**The Electrochemistry Model**

This model computes the local current density \( i(x) \) given the load potential. It makes the following assumptions. First, the flow of oxygen-ion current through the electrolyte is assumed to be one-dimensional, across the electrolyte from the anode to the cathode. Second, the electrochemistry consists only of the reduction of atmospheric oxygen at the cathode, and the oxidation of hydrogen at the anode. Although \( \text{H}_2 \) and \( \text{CO} \) are both electrochemically active fuels, there is strong evidence that on the anode side, \( \text{H}_2 \) dominates the charge-transfer chemistry, and water-gas-shift chemistry replenishes the \( \text{H}_2 \) via reaction of \( \text{CO} \) with the \( \text{H}_2\text{O} \) that is a product of the \( \text{H}_2 \) charge transfer (9, 14).

By these assumptions, the relationship between current density and potential difference
can be derived. Detailed discussion can be found in references (5, 6) by Zhu and Kee. In brief, the current density $i(x)$ is solved from

$$E = E^0 - \eta_{\text{hom}}(i) - \frac{L_s i}{\sigma(T)} - \eta_{\text{act,e}}(i) - \eta_{\text{act,a}}(i) \quad [11]$$

by Newton iteration with charge-transfer overpotentials $\eta_{\text{act,a}}$ and $\eta_{\text{act,e}}$ at the electrode-electrolyte interfaces obtained by (numerically) inverting the Butler-Volmer equation (15)

$$i = i_0 \left[ \exp\left( \frac{\alpha_n \eta_{\text{act}}}{RT} \right) - \exp\left( -\frac{\alpha_c \eta_{\text{act}}}{RT} \right) \right] \quad [12]$$

at the anode- and cathode-electrolyte interfaces respectively, where $i_0$ is the exchange current density, $\alpha_n$ and $\alpha_c$ are the anodic and cathodic asymmetric factors for each of the electrodes, $F$ is Faraday's constant, and $R$ is the universal gas constant. $L_s$ and $\sigma$ are the electrolyte thickness and ionic conductivity, respectively.

The exchange current density $i_0$ generally depends on the local composition at the electrode. For cathode oxygen reduction,

$$i_{0,c} = I_c F_{2O} \alpha \quad [13]$$

with $\alpha \approx 0.5$ (6). At the anode,

$$i_{0,a} = I_a F_{H_2} \gamma (F_{H_2O})^\delta \quad [14]$$

with $\gamma = 0.25$ and $\delta = 0.75$. $I_a$ and $I_c$ are taken as empirical parameters, and are taken to be 0.2 A/cm² and 1.5 A/cm² respectively. The non-zero mass fluxes at the electrode-electrolyte interfaces can be computed when $i(x)$ is known. At the anode-electrolyte interface,

$$J_{H_2} = -\frac{i(x) W_{H_2}}{2F}, \quad J_{H_2O} = \frac{i(x) W_{H_2O}}{2F} \quad [15]$$

and at the cathode-electrolyte interface

$$J_{O_2} = -\frac{i(x) W_{O_2}}{4F} \quad [16]$$

where $W_k$ is the molecular weight for species $k$. These fluxes are used as boundary conditions for the porous electrode transport model.

**The Conduction and Radiation Model**

This model predicts the cell temperature, which is a crucial factor for the electrical performance since it dictates reaction rates and electrolyte conductivity. Shao et al. found experimentally that the cell runs typically 150°C higher than the furnace temperature.
when the latter is around 650°C. Therefore a complete model must be able to predict this trend.

Figure 2 shows schematically the energy exchange processes, including conduction within the cell, enthalpy changes at the electrodes, and radiation heat exchange between the cell and the furnace. We assume the conduction is 1-D in the x direction, because the thickness of the cell is much smaller than its length, and the thermal conductivity is high. The energy balance over a control volume of dimensions $\Delta x$ and $\Delta y$ in the cell is formulated as

$$\rho C_{pa} \frac{\partial T}{\partial t} \Delta x \Delta y = (q_{\text{left}}^n + q_{\text{right}}^n) \Delta y - i \cdot E \cdot \Delta x$$

$$+ \{(-\Delta H)_a + (-\Delta H)_c\} \Delta x - (q_{Ra}^n + q_{Rc}^n) \Delta x$$

where $q_{\text{left}}^n$ and $q_{\text{right}}^n$ are respectively the conduction heat fluxes across the left and right faces, $\Delta H$ is the enthalpy change, and $q_{Ra}^n$ is the net radiation heat flux to the furnace, with subscripts “a” and “c” indicating the anode and cathode, respectively. The control volumes coincide with the flow model grid for scalar variables.

For non-isothermal computation, this model is enabled. In this case, we assume there is only one cell in the gas channel, and the furnace has a uniform, specified temperature. The cell temperature is supplied to the flow model as the boundary condition for the energy equation [4].

**Software Implementation**

The flow model and the conduction and radiation model are both implemented in Fortran 90 using a CANTERA (4) interface. The electrochemistry model is written in C++ and also interfaced to CANTERA.

**RESULTS AND DISCUSSION**

The model is capable of simulating many different SCFC configurations. Figure 3 shows a gas channel with one cell. However, multiple cells can be placed in the channel. At present, multiple cells are only supported in isothermal simulations. Here we only discuss one cell for...
simplicity. The channel height is 15.875 mm, and the length is 9 times the height. The temperature is taken to be 800°C (isothermal), and the pressure is one atmosphere. The thicknesses of anode, cathode and electrolyte are 700, 10 and 15 microns respectively. This example explores the influence of fuel-to-oxygen ratio and carrier gas on the SCFC electrical performance. As shown in Figure 3, the mixture of methane, oxygen and carrier gas (nitrogen or helium) comes in from the left. The flow rate of methane is fixed at 87 sccm (ml/min at standard conditions), and the ratio of oxygen to carrier gas is fixed at 1 to 4. A small amount of hydrogen and water is present at the inlet. The gas mixture is assumed to be fuel-rich, and the load potential is taken at 0.5 V. The simulation is run until steady state is achieved.

Figure 4 shows the dependence of the power density on the fuel-to-oxygen ratio with two different carrier gases. For both cases, the optimum ratio is around 2. Figure 5 shows the mole fractions of all the gas-phase species at the anode-electrolyte interface, plus that of oxygen at the cathode-electrolyte interface at the middle of the cell, with helium being the carrier gas. Since hydrogen and oxygen are the two reactants for electrochemistry at the anode and cathode respectively, the peak power density should occur where both reactants are present in sufficient concentrations, i.e., around the intersection of the two curves. This intersection corresponds to ratio 1.47 for helium, and 1.63 for nitrogen, which agrees with the trend of the peak power density location. Trends at other locations along the cell are similar. Figure 6 shows the polarization curves at the optimum oxygen flow rates. From figures 4 and 6, we see that an SCFC has better electrical performance when using helium as the carrier gas. This occurs because helium improves the diffusion coefficient of the gas mixture. This conclusion is in agreement with the observations of Shao et al. with both methane and propane as the fuel.
CONCLUSIONS

We have developed a 2D model for single-chamber SOFC operating on hydrocarbon fuels. It provides insights into factors responsible for SCFC performance. Predicted trends are in good agreement with experiment results. The model can be applied to study mechanistic issues of SCFC operation, as well as optimization of the SCFC stack design.

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