MODELLING THE POWER REDUCTION IN SOFC DUE TO HOT SPOTS

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ABSTRACT

The KAMELEON SOFC SIM computer code was further developed in order to find simultaneous solutions of all conservation equations for mass, energy and momentum in a quasi three dimensional flat plate, solid oxide fuel cell. Cell performance was simulated numerically for cells with and without cracks in the ceramic plate. Standard data sets were used in the simulation. A substantial power reduction was observed when cracks, leading to hot spots, were formed. The direct combustion was modelled as laminar diffusion flames. We found that the flame front was located at the air side of the ceramic plate. The position of the crack was important for formation of water in the air channel. The power reduction in the cell therefore depended largely on the position of the crack in the plate.

INTRODUCTION

The ceramic components of a Solid Oxide Fuel Cell (SOFC) are exposed to external and internal stresses during fabrication and operation. Because ceramics are brittle, cracks can be generated during fabrication (1). Even at very low stress levels, all ceramic materials show a slow crack growth, leading to catastrophic failure after a certain time (2). Until now, most works have been devoted to the study of SOFCs running at ideal operating conditions, i.e. SOFCs without any defects. Calculations related to cracks and hot spots in different parts of the cell are not reported to our knowledge.

In this paper we present further results from a numerical method for calculating conditions in a single cell during operation. This includes the flow field, pressure field, temperature field, distribution of mass fractions of the different chemical species, and the electric potential field. We have previously used this method to establish pressure gradients as well as transverse and longitudinal temperature gradients in the SOFC (3). The simulations of flawless cells showed that the static pressure gradient had local maxima below the current collectors (ribs) of the single cell; the highest value was below the first rib. The temperature gradients were severe in both directions, in particular in the
region close to the entrance. We therefore concluded that the most probable crack location was close to the first rib. The aim of this work is to present a numerical method which can examine how cracks influence the performance of the SOFC.

The reactants enter a direct combustion reaction when leakage is allowed. The heat effect associated with this combustion is positive and large, it is the enthalpy of the reaction. This leads to so-called hot spots in the cell. The heat effect associated with the electrochemical reaction is, on the other hand, given by the entropy of reaction. Increased temperature gradients from hot spots may enhance the probability for further cracks in the thin and brittle electrolyte. It is therefore important to control the formation of such spots.

We shall assume here that the combustion reaction is infinitely fast. This implies that no oxygen exists on the fuel side of the flame, and that no fuel exists on the oxygen (air) side. This is probably a good assumption, considering the reactivity of hydrogen. The present work can be regarded as a first attempt to obtain a simultaneous solution for the different transport processes, electrochemical reaction and combustion reactions in SOFC. The crack shall first be located directly below the first rib, and next just outside the same rib. Only one crack is calculated at a time.

SINGLE CELL DESCRIPTION

The single cell geometry and the control volumes (CV) are shown in Figs.1 and 2. The system is quasi three-dimensional (the z-component of the velocities are zero). There is hydrogen in the fuel channel in the bottom of Fig.2, and air in the other channel. The ceramic plate between the channels is 500 µm thick. It consists of the 200 µm thick electrolyte (ZrO₂ with 8 mol% Y₂O₃), the 150 µm thick Ni anode and the 150 µm thick perovskite cathode. Electric current produced by the electrode reactions is collected by six ribs. The electronic conductivity of the ribs is 3100 S/m.

Simulations are run for rib thickness 1.5 mm. The ribs are neglected in the calculations of bulk gas properties. Their impact is mainly on the current production. There are 100 CVs in the x-direction over 5 cm, while the number of CVs in the y-direction are 22 (irregular spacing over 7.5 mm). A close-up of the CVs around the electrolyte is shown in Fig.3.

The crack was defined by two CVs. The open space in Fig.3. show the position of the first crack. The other crack was shifted two control volumes to the right (not shown). To take into account that the crack is smaller in size than the control volume, we adjusted the transport properties of the electrolyte in the CVs. This approach allowed us to model ionic, electronic and gas transport through the same CV, in opposite directions, if necessary.
The cell reaction can be written by three steps:

\[
\begin{align*}
\frac{1}{4} O_2(y_2) + e &= \frac{1}{2} O^2(y_2) \\
\frac{1}{2} O^2(y_2) &= \frac{1}{2} O^2(y_1) \\
\frac{1}{2} H_2(y_1) + \frac{1}{2} O^2(y_1) &= \frac{1}{2} H_2O(y_1) + e
\end{align*}
\]

(1)

The locations are \( y_1 = 2.000 \text{ mm} \) and \( y_2 = 2.500 \text{ mm} \).

**MATHEMATICAL MODEL AND SOLUTION PROCEDURES**

The conservation equations for mass, energy and momentum, are written on the same form for the gas mixtures and the solid materiales in KAMELEON SOFCSIM (4).

*Momentum conservation* applies to the gas phases having mass density \( \rho \), pressure \( p \) and dynamic viscosity \( \mu \). From Navier-Stokes equations, we have for the velocity components \( u \) and \( v \) of the mean mass velocity that:

\[
\begin{align*}
\frac{\partial}{\partial t} \rho u + \frac{\partial}{\partial x} (\rho u u) + \frac{\partial}{\partial y} (\rho u v) &= \frac{\partial}{\partial x} (\mu \frac{\partial u}{\partial x}) + \frac{\partial}{\partial y} (\mu \frac{\partial u}{\partial y}) - \frac{\partial p}{\partial x} \\
\frac{\partial}{\partial t} \rho v + \frac{\partial}{\partial x} (\rho u v) + \frac{\partial}{\partial y} (\rho v v) &= \frac{\partial}{\partial x} (\mu \frac{\partial v}{\partial x}) + \frac{\partial}{\partial y} (\mu \frac{\partial v}{\partial y}) - \frac{\partial p}{\partial y} - \rho g
\end{align*}
\]

(2)

(3)

*Mass conservation in the gas mixtures* can be written as:

\[
\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x} (\rho u) + \frac{\partial}{\partial y} (\rho v) = 0
\]

(4)

Eqs.(2-4) are used for calculations of the static pressure.

*Mass conservation for a component* is fulfilled for each CV in the gas phase. The mass fraction, \( m_\lambda \), is calculated for every chemical species, \( \lambda \), from:

\[
\frac{\partial}{\partial t} (\rho m_\lambda) + \frac{\partial}{\partial x} (\rho u m_\lambda) + \frac{\partial}{\partial y} (\rho v m_\lambda) = \frac{\partial}{\partial x} (\rho D_\lambda \frac{\partial m_\lambda}{\partial x}) + \frac{\partial}{\partial y} (\rho D_\lambda \frac{\partial m_\lambda}{\partial y}) + m_\lambda
\]

(5)

where \( D_\lambda \) is the diffusion constant. The source term for the mass, the last term of Eq.(5), is mainly connected to the electric circuit. For the CVs in the electrodes we have:

\[
m_{\text{an}}(y_2) = m_{a_1} = -\frac{M_{o_1} j}{4F}
\]

(6)

\[
m_{\text{cat}}(y_1) = m_{c_1} + m_{H_2O} = (-M_{H_1} + M_{H_2O}) \frac{j}{2F}
\]

(7)
The anode has subscript an, while the cathode has subscript cat. Molar masses are given the symbol $M$. The flux of $O_2^*$ across the electrolyte defines the electric current density, $j$. We assume that the chemical reaction is faster than fuel and oxygen transport to the reaction zone, i.e. we are dealing with a diffusion controlled process.

In addition we have source terms due to direct combustion where hot spots are made.

The heat balance equation for the mixture is:

$$\frac{\partial}{\partial t}(\rho T) + \frac{\partial}{\partial x}(\rho u T) + \frac{\partial}{\partial y}(\rho v T) = \frac{\partial}{\partial x}(k \frac{\partial T}{\partial x}) + \frac{\partial}{\partial y}(k \frac{\partial T}{\partial y})$$

$$+ \rho \sum_A D_A \frac{\partial m_A}{\partial x} \frac{\partial T}{\partial x} + \frac{\partial m_A}{\partial y} \frac{\partial T}{\partial y} + \dot{q} - \sum_A h_A \dot{m}_A$$

(8)

Here $c_p$ is the specific heat capacity, $T$ is the temperature, $k_x$ and $k_y$ are the Fourier type heat conductivities, and $h_A$ is the enthalpy of reaction for species $A$.

The first source term, $\dot{q}$, relate to the heat effects in electrochemical systems. In the electrode compartments, where these terms are relevant, there are reversible heat changes rigidly connected with an entropy change derived from Eqs.(6-7) plus an irreversible heat production due to reaction overpotentials. For the CVs of the electrodes we have

$$\dot{q}_{cat} = T_{cat}(\frac{1}{4}S_{O_2} - \frac{1}{2}S_{O^2-} - S_{el}^*) \frac{j}{F} + \eta_{cat} \frac{j}{F} + \frac{1}{\sigma_{cat}} j^2$$

(9)

$$\dot{q}_{an} = T_{an}(\frac{1}{2}S_{H_2O} + \frac{1}{2}S_{H_2} + \frac{1}{2}S_{O^2-} + S_{el}^*) \frac{j}{F} + \eta_{an} \frac{j}{F} + \frac{1}{\sigma_{an}} j^2$$

(10)

where $S_A$ are molar entropies of the components, $S_{O^2-}$ is the transported entropy of the oxygen ion, $S_{el}^*$, the transported entropy of the electrons, and $F$ the Faraday's constant. The overpotentials at the electrodes, which are given the symbols $\eta$, are taken as functions of the partial pressures of the reactants. The electric conductivity of a CV is $\sigma$. The heat effects associated with the electrodes of the solid oxide fuel cell were described in detail previously (5).

For CVs outside the electrodes, Joule heat terms are the only contributions to the heat source terms:

$$\dot{q}_J = \frac{j^2}{\sigma}$$

(11)

Direct combustion in cracks means reactions in the homogeneous gas phase. The last term of Eq.(8) applies. It contains the enthalpy of the gas phase reaction. The source terms have a nonzero value only for the CVs where the flame front exists.
We shall model the homogenous chemical reaction as laminar diffusion flames. The discrete nature of the numerical simulation, means that the flame front will be located somewhere between two grid points (nodes), and that the modelling results in combustion in two adjacent CVs. In the first CV some oxygen and the rest of the hydrogen are consumed, in the other, the rest of the oxygen and some hydrogen are consumed. In all other CVs the sink terms for oxygen and hydrogen are zero.

So far we have implemented the mass conservation equations for the reactions with a zero reaction enthalpy. The purpose of choosing this as a first step is to obtain a reference state for further studies.

Energy conservation in the cell is expressed by combining the first and second law of thermodynamics. This gives an expression for the total availability (maximum theoretical work obtainable from the system), consisting of thermomechanical and chemical availability. The maximum electric power is then the chemical availability per unit time. We call this $P_{\text{max}}$.

Part of the electric power of the cell, $P'$, is lost due to Joule heat in the leads and overpotentials of the electrodes, giving $P = P_{\text{max}} - P'$.

The partial molar enthalpies and entropies are combined for each component to the respective chemical potential, $\mu_i$. The electric work of the cell, $P = E_j$, generated between the electrodes, is then:

$$E_j = \left[\frac{1}{2}\mu_{H_2O}(T_{an}) - \frac{1}{2}\mu_{H_2}(T_{an}) - \frac{1}{4}\mu_{O_2}(T_{an})\right] + \left(\eta_{\text{cat}} + \eta_{\text{an}}\right)j + \sum \left(\frac{1}{\sigma_j}\right) j^2 \quad (12)$$

The overpotentials $\eta$ of the electrodes are dealt with by summing over the ohmic resistance and a contribution from the concentration gradients, proportional to the partial pressure of the reactants. $\sigma_j$ is the electronic conductivity of the control volumes. For further details, see (3).

**CALCULATION PROCEDURES**

Standard cell materials were chosen. Values for thermodynamic and transport properties were taken from Bossel and Ferguson (6). The transported entropies were $S'_{\text{O}_2} = 42 \text{ J/K mol}$ and $S'_{\text{H}_2} = -1 \text{ J/K mol}$ (10). The inlet gas temperature was set to 850°C for both air and fuel. Inlet gas velocities were 0.05 m s$^{-1}$ for H$_2$ and 0.25 m s$^{-1}$ for air. At $x = 50 \text{ mm}$ we have $dT/dx = 0$, $dm_i/dx = 0$ and $p = 1$ bar for both mixtures. Adiabatic surfaces were chosen for the solid materials to simulate their conditions in a stack.

The calculations were limited to steady state conditions, so time derivatives in the equations were set to zero. The KAMELEON SOFCSIM program gives a simultaneous

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solution of all nine dependent variables \((u, v, p, T, m_A, E)\) as functions of \(x\) and \(y\) in the cell. The numerical solution uses the finite volume method described by Patankar (7). The velocity field was calculated from a staggered grid. The SIMPLER algorithm was used to obtain the static pressure field (7).

A cell potential of 0.6 V between the surfaces at \(y=0\) and \(y=7.5\) mm, was used as a boundary condition for Eq.(12). The assumption of a constant voltage can be justified when the electric conductivity of the electrolyte with electrodes is high, and the reaction rates also are high. The electric potential between cathode and anode was calculated from Eq.(12). Instead of having a potential jump at the electrolyte/anode interface (8), the Nernst potential was distributed evenly to all faces between the cathode and anode. The electric potential thus had contributions from the cathode and the anode. The ionic and electronic currents were also calculated. The electronic short circuit from the anode to the cathode is needed to find cell operating conditions at zero power output.

RESULTS AND DISCUSSION

Simultaneous solutions of Eqs.(1-12) are presented graphically in Figs.2-5.

Gas velocity fields for fuel and air were obtained as shown in Fig.2. The maximum pressure difference across the electrolyte with this field was close to 100 Pa, the lower pressure being below the ribs on the air side. In the case that a crack appears, this difference implies that oxygen leakage by bulk flow into the fuel channel is excluded. Oxygen may, however, diffuse into the fuel channel. Hydrogen may immediately leak into the air channel. It is the result of this leak we report below.

Composition variations that are simultaneous with the velocity fields of Fig 2. are shown by a close-up view in Fig.3. We see that oxygen and hydrogen conversion takes place along the channel. Of special interest are the current density arrows of Fig.3. The presence of a crack reduces the electric current, not only in the CVs of the crack, but there is an immediate impact also on the neighboring control volumes. The current produced by the cell is reduced (not shown).

The mass fractions of the product formed by the reaction, water, in Fig.4, show the expected behaviour for a crack. The product is formed in the air channel and is carried away by bulk flow and diffusion. Notice the visible effect of diffusion upstream. The calculations show that with the existing velocity field, the water from the combustion reaction is formed at the border facing the air channel, not inside the crack.

We have assumed that a laminar diffusion flame will develop from the leakage that we have introduced in the electrolyte. This implies that the flame front will be situated at the position of the so-called stoichiometric surfaces in the gas phase. This is the loca-
tions where we find a stoichiometric mixture of air and fuel. The combustion zone is extremely thin (a flame front), and the chemical reaction is fast. A major problem in the calculations is therefore to locate the stoichiometric surface. This was successfully performed by the present simulation: The location obtained was as expected; at the interface to the air channel (Fig. 3).

The power reduction which follows the crack is 3% when the crack is directly below the rib, but 39% when the position is shifted slightly to the right of the rib. The numerical solution of the equations provide a value for \( j \) which varies in an expected manner. The value decreases as the Nernst potential across the cell is reduced. This also lends credibility to the simulated results. Considering the assumptions involved in the calculations these numbers should not be taken as real, however. The conclusion that can be drawn from the analysis is at present that the position of the crack is very important for the power reduction.

The thermal consequences of the combustion are, of course, central. As a start to approach this problem we have chosen to use an enthalpy of reaction equal to zero. This is because we wanted to find the flame position, as described above, in a well defined situation. By achieving this aim, we may deduce that the numerical calculation procedure is good. Because of the strong exothermic nature of the reaction, we may eventually expect a flame temperature which is very high. As a next step in our work we shall study this effect. We may already conclude from the distribution of reactants that cracks may significantly alter the temperature gradients in a flawless cell.

Fig. 5 shows the temperature gradients corresponding to the solutions presented in Figs. 2-4. We see that the temperature varies significantly in the \( x \)-direction, and that the velocity field has a major impact on the temperature field in the gas phase (Figs. 2 and 4). Temperature gradients in the solid state materials were calculated for the \( x \)-direction. A variation of 3000 K m\(^{-1}\) over the first cm was obtained. This is according to the discussion above, obtained for a zero reaction enthalpy. We expect large variations in this picture when realistic values can be used for the reaction enthalpy.

How the hot spots develop, which temperature they will achieve, how they influence the cell performance, and at last which safety risk they represent, are all important questions to answer. These are topics for future investigations, when more knowledge is gained, e.g. on thermal stresses. We shall also improve our theoretical equations for the surface potentials.

From our study a detailed picture of the cell events emerged. The results of Figs. 2-5 produced the major effects that we must expect from the cell reaction, like the consumption of fuel and production of heat. But in addition to the major effects, we also saw effects on crack behaviour on a \( \mu \)m length scale. The finer details produced by the solution, is of particular interest since these are results which cannot be obtained in a
reliable manner by methods which make simplifying assumptions in the outset. Experimental results of the same are expensive.

CONCLUSIONS

We have demonstrated the successful application of a numerical simulation method which is able to model direct combustion in cracks in SOFC. Some input data have been simplified and assumptions have been introduced; therefore the results are only qualitative. The power reduction due to cracks, the position of the flame front, and the importance of the crack position are likely results, however. We may therefore conclude that the KAMELEON SOFCSIM program is developing to a useful design tool for the single cell of SOFC.

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**FIGURES**

![Fig.1](image1.jpg)

Fig.1. Schematic illustration of the single cell, with 27x24 grid points and 25x22 control volumes. The length of the channel is 50 mm while the heigh is 7.5 mm.

![Fig.2](image2.jpg)

Fig.2. Gas velocities (given as arrows) in the control volumes of the single cell. The finer grid (100x22 control volumes) is used.
Fig. 3. The position of the crack below the first rib in the single cell. Mass fractions of oxygen and hydrogen in the cell and electric current (given as arrows) are also shown in this close-up.

Fig. 4. Mass fraction variations of water in the single cell with a crack.

Fig. 5. Temperature profiles in the gases of the fuel cell. Inlet temperature is 850°C.