GAS FLOW AND HEAT TRANSFER WITH INTERNAL REFORMING REACTIONS IN AN ANODE DUCT OF SOFCs

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ABSTRACT

A fully three-dimensional calculation method has been further developed to simulate and analyze internal reforming and its effects on various processes in a thick anode duct. In this study, the composite duct consists of a porous anode, the flow duct and solid current connector. Momentum and heat transport together with gas species equations have been solved by coupled source terms and variable thermophysical properties (such as density, viscosity, specific heat, etc.) of the fuel gas mixture. The fuel cell conditions such as the combined thermal boundary conditions on solid walls, mass balances (generation and consumption) associated with the reactions and gas permeation to/from the porous electrode are applied in the analysis. Simulation results show that the internal reforming reactions are significant to fuel gas transport and heat transfer in the anode.

INTRODUCTION

One of the trends during recent years is to reduce the operating temperature of solid oxide fuel cells (SOFCs) to a moderate range (700–900°C) by employing a thick porous layer (1.5–2 mm) as the supporting structure (1-4). For this new design, the size of the porous anode is bigger than that of the flow duct in terms of thickness and cross-sectional area. The transport rate of fuel gases to active sites for electrochemical reactions is controlled by various parameters, such as porous microstructure (e.g., pore size, permeability, volume percent porosity), pressure gradient between the flow duct and porous layer, gas composition and inlet conditions, etc (5-7). When pure hydrogen is employed as a fuel, part of it is consumed while water vapor (H₂O) is generated during the electrochemical reaction. This is simulated as a mass suction and injection $V_m$ (or $Re_m = V_m D_h / \nu$), respectively, at the permeable wall in the anode side (6, 7).

It is a fact that the heat required for steam reforming can be provided by the electrochemical reactions in SOFC stacks when fuelled with hydrocarbon fuels. It is one of advantages of SOFCs, because the cooling required by the fuel cell (usually achieved by flowing excess air through the cathode in the case of external reforming systems) will be much smaller for internal reforming system. Then, the energy conversion efficiency will be much higher, and this benefit does not appear when pure hydrogen is considered as the fuel. Moreover, close coupling of the internal reforming and the electrochemical reactions at the anode gives good heat transfer. Furthermore, hydrogen and CO are utilized by the cell as soon as they are produced by the reforming reaction, and the steam...
produced by the electrochemical reaction can be used in the reforming reaction as well (8). However, most of the internal reforming reaction takes place in the anode next to the flow duct due to the high methane conversion rate, and very little methane reaches the active surface between the electrolyte and porous anode. The endothermic reforming reaction and the exothermic electrochemical reactions are separated, and consequently lead to big temperature gradients in the porous layer. There is a need to deeply understand the reaction mechanisms and effects on the transport processes in the duct.

To extend our previous studies (5-7), a fully three-dimensional numerical investigation has been further developed to include internal reforming reactions in the reduced temperature SOFC anode duct. The duct under investigation includes the porous layer, gas flow duct and the solid inter-connectors. By calculating fuel gas species, the mass/heat generation and consumption related to the internal reforming and the electrochemical reactions have been identified and applied in the study. Moreover, the variable thermal-physical properties of the fuel gas mixture have also been taken into account. The thermal boundary conditions of the fuel cell are employed in the investigation as well. An objective of this paper is to develop such a calculation method to understand the internal reforming reaction and effects on various transport processes in ducts for reduced temperature SOFCs.

PROBLEM STATEMENT AND FORMULATION

Problem Statement and Assumptions

With heat generation by the electrochemical reactions in the SOFC stack, internal reforming of hydrocarbon fuels takes place at the anode of the cells with steam. The section of the anode, where reforming occurs, is adjacent to the place where the electrochemical reaction appears, the heat from the fuel cell electrochemical reactions is supplied for the reforming reaction by internal heat transfer with minimal losses.

Methane and carbon monoxide can be reformed into H₂ by the following reactions:

\[ CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H_{1000} = -226 \text{ kJ/mol} \]  
\[ CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H_{1000} = -35 \text{ kJ/mol} \]

Equation [2] is usually referred to as water gas shift reaction. It should be mentioned that the process in Eq. [1] is endothermic and the overall balance of the reaction requires net heat input by the electrochemical reaction.

The electrochemical reactions to generate electricity are the oxidation of H₂ and CO:

\[ H_2 + O^{2-} \rightarrow H_2O + 2e^- \]  
\[ CO + O^{2-} \rightarrow CO_2 + 2e^- \]

The above reactions produce a significant amount of the water at the anode side during operation.
A three-dimensional computational fluid dynamics (CFD) code is employed for an anode duct of a typical reduced temperature SOFC design, see Fig. 1a. A schematic structure of the anode duct is shown in Fig. 1b. The $U$, $V$, and $W$ are the velocity components in the $x$, $y$, $z$ directions, respectively. In this study, the porous anode layer is assumed to be homogeneous and characterized by effective parameters and the fuel in the porous layer is in thermal equilibrium with the solid matrix. The electrochemical reaction appears at the interface between the electrolyte and the porous layer (bottom surface in Fig. 1b), while the internal reforming reactions are within the porous layer. A constant flow rate $U=U_{in}$ with a mass fraction of the mixed fuel is specified at the inlet of the gas flow duct, while $U=0$ is specified at the inlet for the inter-connector and porous anode layer. Only the right half of the duct is considered by imposing symmetry conditions on the mid-plane.

![Figure 1.](image)

**Figure 1.** a) Structure of a unit cell; b) schematic drawing of a composite anode duct.

**Governing Equations**

The governing equations to be solved are the continuity, momentum, energy and species equations. The mass continuity equation is written as

$$\nabla \cdot (\rho_{\text{eff}} \mathbf{V}) = S_m$$  \[5\]

The source term $S_m$ in the above equation accounts for the mass balance due to the electrochemical reactions.

$$S_m = (J_{H_2} \times J_{CO} \times J_{H_2O}) \frac{A_{\text{active}}}{V} = (-\frac{i_{CO}}{2F} M_{H_2} \frac{i_{CO}}{2F} M_{CO} + \frac{i_{H_2} + i_{CO}}{2F} M_{H_2O}) \frac{A_{\text{active}}}{V}$$  \[6\]

where $V$ refers to control volume, and $(i_{H_2} + i_{CO})$ is the total current density $i$ passing through the cell. The momentum equation reads

$$\nabla \cdot (\rho_{\text{eff}} \mathbf{V} \mathbf{V}) = -\nabla P + \nabla \cdot (\mu_{\text{eff}} \nabla \mathbf{V}) + S_{\text{di}}$$  \[7\]

The inclusion of the source term $S_{\text{di}}$ allows Eq. [7] to be valid for both the porous layer and the flow duct:

$$S_{\text{di}} = -(\mu_{\text{eff}} \nabla \beta \cdot \mathbf{V}) - \rho_{\text{eff}} BV_1 |\mathbf{V}|$$  \[8\]
The first term on the right hand side of the above equation accounts for the linear relationship between the pressure gradient and flow rate according to Darcy's law. The second term is the Forchheimer term which takes into account the inertial force effects, i.e., the non-linear relationship between pressure drop and flow rate (7). In Eq. [8], \( \beta \) is the porous layer permeability, and \( \mathbf{V} \) represents the volume-averaged velocity vector of the species mixture. For example, the volume-averaged velocity component \( U \) in the \( x \) direction is equal to \( \varepsilon U_p \), where \( \varepsilon \) is the porosity, \( U_p \) the average pore velocity (or interstitial velocity). It should be noted that Eq. [7] is formulated to be generally valid for both the flow duct and the porous layer, i.e., the source term is zero in the flow duct, because the permeability \( \beta \) is infinite. Equation [7] then reduces to the regular Navier-Stokes equation. For the porous layer, the source term Eq. [8] is not zero, and the momentum Eq. [7] with the non-zero source term can be regarded as a generalized Darcy model (7).

The energy equation can be expressed as

\[
\nabla \cdot (\rho_{\text{eff}} C_{\text{peff}} \nabla T) = \nabla \cdot (k_{\text{eff}} \nabla T) + S_T
\]

where \( S_T \) is the heat source associated with the internal reforming reactions,

\[
S_T = R_{ir} h_{ir}
\]

\( R_{ir} \) is the reaction mass flux by the internal reforming, and \( h_{ir} \) is the reaction enthalpy. The species conservation equations are formulated in a general form,

\[
\nabla \cdot (\rho_{\text{eff}} \nabla \phi) = \nabla \cdot (\rho_{\text{eff}} D_{\phi, \text{eff}} \nabla \phi) + S_{\phi}
\]

where \( \phi \) is the mass fraction of the fuel gases. The above equation is solved for \( \text{H}_2, \, \text{CH}_4, \, \text{CO} \) and \( \text{H}_2\text{O} \), respectively. The concentration of the inert species, \( \text{CO}_2 \), is determined from a summation of the mass fractions of the other species. As revealed in (4), the shift reaction in Eq. [2] is very quick and remains in equilibrium, and a quasi homogeneous model of the steam reforming kinetics is assumed in this study:

\[
R_{ir} = k_{ir}^{+} P_{\text{CH}_4} P_{\text{H}_2\text{O}} - k_{ir}^{-} P_{\text{CO}} (P_{\text{H}_2})^3
\]

in which \( k_{ir}^{+} \) and \( k_{ir}^{-} \) are velocity constants of the forward and backward steam reforming reaction, and \( p \) is partial pressure. Then, \( S_{\phi} \) in Eq. [11] reads:

\[
S_{\text{H}_2} = 4 R_{ir} M_{\text{H}_2}; \quad S_{\text{CH}_4} = -R_{ir} M_{\text{CH}_4}; \quad S_{\text{H}_2\text{O}} = -2 R_{ir} M_{\text{H}_2\text{O}}; \quad S_{\text{CO}_2} = R_{ir} M_{\text{CO}_2}
\]

In the above equations, all parameters with subscript \( \text{eff} \) are the effective ones, and reduce to the values of the fuel gas mixture in the flow duct based on the composition of \( \text{H}_2, \, \text{CH}_4, \, \text{CO, H}_2\text{O and CO}_2 \). For simplicity, the properties such as density and viscosity in the porous layer are simply evaluated by \( \rho_{f} \) and \( \nu_{f} \) of the species mixture (\( \text{H}_2+\text{CH}_4 +\text{CO+H}_2\text{O+CO}_2 \)), respectively. However, the effective conductivity \( k_{\text{eff}} \) and effective...
diffusion coefficients are estimated by employing various values for the ratios \( \theta \) to considering the porous layer effects (2, 9), i.e.,

\[
\theta_k = \frac{k_{\text{eff}}}{k_f} \quad \text{[14]}
\]
\[
\theta_D = \frac{D_{\text{eff}}}{D_\phi} \quad \text{[15]}
\]

where \( \theta_D \) is diffusion coefficient ratios, \( D_\phi \) is species diffusion coefficients. By varying the property ratio, the corresponding effective property in the porous layer sub-domain can be different from that of the species mixture, if the property ratio is not equal 1.

**Boundary and Interfacial Conditions**

Based on the fuel cell function, the thermal and fuel gas mass concentration/flux boundary conditions at the walls are as follows:

\[
U = V = W = 0, \quad -k_{\text{eff}} \frac{\partial T}{\partial y} = q_b, \quad -\rho_{\text{eff}} D_{\phi,\text{eff}} \frac{\partial \phi}{\partial y} = J_\phi \quad (\phi = \text{H}_2, \text{CO and H}_2\text{O}) \text{ and} \]
\[
J_\phi=0 \quad (\phi = \text{CH}_4 \text{ and CO}_2) \quad \text{at the bottom wall (} y = 0 \text{) \quad [16]}
\]
\[
U = V = W = 0, \quad q=0, \quad J_\phi=0 \quad \text{at the top and side walls \quad [17]}
\]
\[
\frac{\partial U}{\partial z} = \frac{\partial V}{\partial z} = W = \frac{\partial T}{\partial z} = \frac{\partial \phi}{\partial z} = 0 \quad \text{at the mid-plane (} z=a/2 \text{) \quad [18]}
\]

In the present investigation, the interfacial boundary conditions, commonly employed in the literature and including the continuity of velocity, shear stress, temperature, heat flux, mass fraction and flux, are applied as follows:

\[
U = U_+, \quad (\mu_{\text{eff}} \frac{\partial U}{\partial y})_+ = (\mu \frac{\partial U}{\partial y})_+ \quad \text{[19]}
\]
\[
T = T_+, \quad (k_{\text{eff}} \frac{\partial T}{\partial y})_+ = (k \frac{\partial T}{\partial y})_+ \quad \text{[20]}
\]
\[
\phi = \phi_+, \quad (\rho_{\text{eff}} D_{\phi,\text{eff}} \frac{\partial \phi}{\partial y})_+ = (\rho D_{\phi,f} \frac{\partial \phi}{\partial y})_+ \quad \text{[21]}
\]

Here subscript + (plus) stands for fluid side, and - (minus) for porous layer side. Moreover, the thermal interfacial condition Eq. [21] is also applied at an interface between the porous media and the solid current inter-connector with \( k_t \) instead of \( k_f \).

**NUMERICAL SOLUTION PROCEDURE**

A three-dimensional CFD code was used to solve the governing Eqs. [5, 7, 9, 11], together with the boundary conditions [16-18] and interfacial conditions [19-21]. The code is a general purpose one and based on the finite-volume technique with boundary fitted coordinates for solving the differential equations. The Cartesian coordinate system in the physical space is replaced by a general non-orthogonal coordinate system. The momentum equations are solved for the velocity components on a non-staggered grid.
arrangement. The Rhie-Chow interpolation method is used to compute the velocity components at the control volume faces. Algorithms based on the TDMA and a modified SIP are employed for solving the algebraic equations. In this study, the convective terms are treated by the QUICK scheme, while the diffusive terms are treated by the central difference scheme. The SIMPLEC algorithm handles the linkage between velocities and pressure.

As shown above, the equations needed for the calculation are coupled by current density, temperature, partial pressure / concentration of gas species via source terms and thermal-physical properties. It should be noted that the source term in Eq. [5] is zero in most of the regions, and non-zero only in the regions neighboring boundaries, where mass transfer caused by the electrochemical reaction occurs (bottom wall in Fig. 1b). It is clear that no gas flow is present in the solid inter-connector. Equations [5], [7] and [11] are then blocked out and only the heat conduction equation, derived from the energy Eq. [9], is solved for this domain. As mentioned earlier, the thermal-physical properties of the fuel gas mixture are variable. These parameters depend on the position in the duct, and the species mass fraction and / or temperature as well. Fuel gas mixture density, viscosity and specific heat capacity are then calculated and updated during the calculation.

Parameters of the reduced temperature SOFCs and the porous medium, appearing in the literature, are applied as a base case in this study. Duct geometries are employed as follows: length of the duct \( L = 20 \text{ mm} \); width of the porous layer \( a = 2 \text{ mm} \), and its thickness \( h_p = 2 \text{ mm} \); while the width of the flow duct is \( b = 1 \text{ mm} \), and its height \( h_d = 1 \text{ mm} \). Fuel gas inlet temperature \( T_{in} = 800 \ ^\circ\text{C} \); effective diffusion coefficients are: \( D_{H_2} = 9.5 \times 10^{-5} \text{ m}^2/\text{s} \), \( D_{CH_4} = 2.8 \times 10^{-5} \text{ m}^2/\text{s} \), \( D_{H_2O} = 3 \times 10^{-5} \text{ m}^2/\text{s} \), \( D_{CO} = 2.6 \times 10^{-5} \text{ m}^2/\text{s} \); In the porous layer, typical values are employed for conductivity ratio \( \theta_k = 1 \), diffusion coefficient ratio \( \theta_d = 0.5 \) for all the species; porosity \( \varepsilon = 0.5 \) and permeability \( \beta = 2 \times 10^{-10} \text{ m}^2 \); partially (30%) prereformed methane/steam (33/67 vol%/vol%) mixture is supplied at the inlet with: \( Re_{in} = 50 \), mole concentration \( \text{H}_2: \text{CH}_4: \text{CO}: \text{H}_2\text{O}: \text{CO}_2 = 0.284:0.171:0.028:0.473:0.044 \); The velocity constants of the steam reaction \( k^+_i = 1.03 \times 10^{-5} - 1.98 \times 10^{-8} T + 9.55 \times 10^{-12} T^2 \text{ mol/(m}^3\text{pa}^2\text{s}) \), \( k^-_i = -2.75 \times 10^{-19} + 5.08 \times 10^{-22} T - 2.22 \times 10^{-25} T^2 \text{ mol/(m}^3\text{pa}^4\text{s}). \) In this study, a constant total current density \( \textit{i} = 0.6 \text{ A/cm}^2 \) is prescribed for the base case. It should be noted that all the results presented hereafter are for the base case condition unless otherwise stated.

RESULTS AND DISCUSSION

Axial velocity contours \((U/U_{in})\) are presented for a reduced temperature SOFC anode duct in Fig. 2. As mentioned above, gas flow and heat transfer in the composite ducts are affected by the internal reforming reactions in the porous layer and the electrochemical reactions close to the active surface. Due to the permeation and mass generation/consumption effects, the uniform distribution and the symmetry of the axial velocity associated with a pure forced duct flow does no longer exist, and the position of the maximum contour values shifts away from the central plane \((y/h = 0.625 \text{ in Fig. 2})\). More mass is permeated into the porous anode layer in the entrance area because of the biggest pressure gradient between the flow duct and the porous layer (6). As a consequence, part of the boundary is shifted into the porous anode layer, which can be verified by a change.
of the boundary layer thickness close to the interface in Fig. 2. Because the pressure in the fuel duct will fall due to friction, a decreased pressure gradient along the main stream is expected. Consequently, gas permeation decreases and becomes weaker. It is clear that the axial velocity magnitude of the fuel mixture decreases rapidly in the porous layer.

![Diagram of the boundary layer](image)

**Figure 2.** Dimensionless axial velocity contours ($U/U_m$) along the main flow stream of a reduced temperature SOFC anode duct at the base case condition.

![Diagram of the boundary layer](image)

**Figure 3.** a) CH$_4$ mass concentration; and b) temperature $T$ distribution along main flow direction of a reduced temperature SOFC anode duct at the base case condition.

The internal reforming reaction can be found in Fig. 3a by the methane distribution in the anode duct, particularly in the porous layer. A large amount of CH$_4$ is reacted in the interface region of the porous layer close to the fuel duct, which is reflected by a sharp decrease of CH$_4$ mass concentration. This region is confined only up to around 200-300 $\mu$m into the anode porous layer at most of the stations along the main flow stream, except at the inlet areas where the reactions take place more deeply into the porous anode. There is hardly any methane reaching the active surface after the first 20% of the duct length, see Fig. 3a. It is clear that the temperature increases steadily along the main flow.
The variation in temperature distribution can also be observed in the vertical direction with a slightly larger value close to the active surface. These are created by the heat generation due to the electrochemical reactions close to the active surface. Due to the effects from the net endothermic reforming reactions, a minimum temperature (1°C lower than the inlet temperature) is observed, which is situated in the porous layer close to the fuel duct at the entrance region.

**Figure 4.** a) CO; and b) H₂ mass concentration distribution along main flow direction of a reduced temperature SOFC anode duct at the base case condition.

**Figure 5.** a) H₂O; and b) CO₂ mass concentration distribution along main flow direction of a reduced temperature SOFC anode duct at the base case condition.

CO and H₂ concentration profiles along the main flow stream are shown in Fig. 4a and b, respectively. It can be found that CO concentration decreases steadily along the main flow stream in the porous layer. It is due to the consumption of CO during the electrochemical reaction. Moreover, the gradient of the CO concentration in the direction...
normal to the active surface are larger close to the reaction sites if compared to that close to the interface areas. On the other hand, the active surface is sufficiently supplied with H₂ resulting from the internal reforming reactions. Moreover, the H₂ mass concentration is affected by the mass consumption from the electrochemical reactions, as shown in Fig. 4b.

Water activities in the duct are shown in Fig. 5a. It is observed that H₂O is consumed in the porous anode by the internal reforming reactions. For this reason, mass fractions of H₂O decreases along the main flow direction and to the active surface. However, generation of H₂O by the electrochemical reactions affects the H₂O distribution as well, particularly for the area close to the active surface. A minimum value is found in the porous anode close to the duct exit. As expected, big CO₂ concentrations are observed in the porous anode, based on the CO₂ generation by the internal reforming reactions in the porous layer and the electrochemical reactions close to the active surface.

![Figure 6. CH₄ distribution along the main flow direction of a reduced temperature SOFC anode duct at: a) 900°C; and b) 750°C.](image)

Figure 6 shows the CH₄ mass fraction profiles for various inlet temperatures of the fuel gases. It is found that the CH₄ mass concentration decreases faster in both the main flow and the vertical directions at a higher temperature, i.e., 900°C in Fig. 6a if compared to 750°C in Fig. 6b. It is clear that around 5% methane is not reacted at the low temperature, and reaches the active surface close to the duct exit. However, it is not the case for high temperature in Fig. 6a. It is so because the internal reforming reactions depend on the temperature, i.e., higher temperature causes faster reaction.

CONCLUSIONS

A fully three-dimensional calculation method has been further developed to simulate and analyze gas flow and heat transfer processes in a thick anode duct of SOFCs. The model offers the possibilities of determining temperature and fuel gas species distribution.
profiles by taking into account of the internal reforming reactions and the electrochemical reactions.

In this study, the composite duct consists of a porous anode, the flow duct and solid current connector. Momentum and heat transport together with gas species equations have been solved by coupled source terms and variable thermo-physical properties (such as density, viscosity, specific heat, etc.) of the fuel gas mixture. Results from this study shows that the internal reforming reactions are confined in a thin porous anode area close to fuel flow duct. Transport processes of the fuel gas species and temperature distribution are affected by the reactions. Higher temperature is favor to faster reforming reactions.

ACKNOWLEDGEMENT

This research is financially supported by the National Fuel Cell Programme of the Swedish Energy Agency.

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