GAS TRANSPORT IN POROUS ELECTRODES OF SOLID OXIDE FUEL CELLS

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ABSTRACT

Concentration polarization is a key SOFC performance parameter. It is caused by the limitation of transport of fuel or oxidant from the gas feeding channels through the electrodes to the reaction sites along the electrode/electrolyte interface. This paper presents the numerical simulations of gas transport in the porous electrodes of solid oxide fuel cells with an interdigitated flow channel design. By creating a convective component of mass transport in the porous electrodes, the interdigitated flow channel design could enhance the mass transport. The mass transport simulation was conducted using the FEMLAB software. Two porous media mass transport models, i.e. Fick’s Model and the Dusty Gas Model (DGM) were used in the simulation. The simple but less accurate Fick’s model is validated against the Dusty Gas Model results. It is found that for a combined diffusive and convective flow in the SOFC porous electrodes, when the fuel concentration is low and the pore size is small, the Dusty Gas Model should be used.

NOMENCLATURE

| Symbol | Description                     |
|--------|---------------------------------|
| I      | Current                         |
| C      | Molar concentration            |
| P      | Pressure                        |
| μ      | Dynamic viscosity              |
| T      | Temperature                     |
| N_i^d  | Diffusion flux                  |
| D_i^d  | Effective binary bulk diffusion coefficient |
| α      | Transfer coefficient           |
| E      | Voltage                         |
| V      | Velocity                        |
| K_p    | Permeability                    |
| R      | Universal gas constant         |
| F      | Faraday’s constant              |
| D_i^e  | Effective diffusivity          |
| D_i^k  | Effective Knudsen diffusion coefficient |
| η      | Polarization                    |
INTRODUCTION

The performance of a fuel cell is often described by its voltage-current (I-E) relationship. At high current density, the losses are dominated by the limitation of transport of the fuel/oxidant to the reaction sites, the so-called concentration or mass transport overpotential. Mass transport in the porous electrode strongly depends on the structure of the porous electrode, such as its porosity, tortuosity and mean pore size. To evaluate the species molar fluxes in a porous media, there are two common approaches (1,2). The first approach focuses on the empty space of the pore network through which the gases pass, such as the Fick's model (FM), while the second approach focuses on the obstacles to the gas motion presented by the solid matrix, the Dusty Gas Model. The Dusty Gas Model considers the porous material as massive and stationary gas molecules reside in the mixture and the Stefan-Maxwell diffusion equations are applied to the mixture.

To study the concentration polarization of a Solid Oxide Fuel Cell (SOFC), especially for the thick supporting electrode, a proper mass transport model must be applied. Veldsink et al. (3) studied the mass transport with chemical reactions in catalyst structures using Fick's model and the Dusty Gas Model. They found that the pressure driven flow could be omitted from the flux expression without significant loss of accuracy. The Fick's law gave accurate transport rate estimates, with only small deviations from the Dusty Gas Model results. For a strong convective flow, due to a large pressure gradient, the simulations demonstrated that only Dusty Gas Model could give accurate results. Suwanwarangku et al. (4) conducted a comparative study using the Fick's law and the Dusty Gas Model. The concentration polarizations of a SOFC anode using binary anode gas mixtures of (H₂-H₂O) and (CO-CO₂) and a multicomponent system of (H₂-H₂O-CO-CO₂) were predicted in a one-dimensional slab geometry. It was found that the current density, the reactant concentration and the pore size are the three key parameters for choosing the proper porous model. The Dusty Gas Model works better for the H₂-H₂O and CO-CO₂ systems, especially under high operating current densities, low reactant concentrations and small pore sizes. Similarly, for a CO-CO₂ system, Fick's model can only be used for a porous electrode with large pore sizes. For multi-component systems, where the flux ratio calculations are complicated and the equal counter current diffusions normally do not exist, the Dusty Gas Model must be used. Krishna (5) investigated the intra-particle diffusion of multicomponent gaseous mixtures in macro-porous and micro-porous materials. Bulk, Knudsen and surface diffusions were handled using a unified, consistent approach. The walls of the porous media were modelled as giant dust molecules and had the status of pseudo-species. In (5), the kinetic gas theories were used to predict the Knudsen diffusion coefficients.

The SOFC flow-field, including feeding channels and the porous electrodes, has a significant influence on the cell performance. In contrast to the very limited SOFC flow channel design activities, a number of novel flow channels have been specifically proposed for the low temperature Proton Exchange Membrane Fuel Cells (PEMFC), to address the PEMFC mass transport and water management problems. One of the novel designs is the interdigitated flow field design, which has been proven very effective by some experimental studies. Wang et al. (6) presented an experimental study of PEM fuel cells with interdigitated flow fields under different operation parameters. Nguyen (7) presented a comparative experimental study of fuel cells with interdigitated flow fields and parallel straight channel flow fields. They demonstrated the superiority of the
interdigitated design. Figure 1 shows the schematic drawing of this design. The flow channels are dead-ended, forcing the gas to flow through the porous diffusion layer. In comparison to the flow in a conventional straight parallel flow field design, the use of the interdigitated fuel/air distributors imposes a pressure gradient between the inlet and the outlet channels, forcing the convective flow of the fuel/oxidant through the porous electrodes. Thus the interdigitated design in effect converts the transport of gases to/from the reaction sites from a diffusion-dominated mode to a forced convection dominated mode. The convective flow through the porous electrode reduces the gas diffusion distance to and from the reaction sites. By having the fuel/oxidant flow over the shoulders of the gas distributor, the electrode active area over the shoulder is used more effectively. The shear force of the gas stream helps remove the water condensate, which is entrapped in the electrode layer, thereby reducing the flooding problem. These advantages extend the PEMFC operable regime to higher current densities and consequently, a 50-100% increase in the fuel-cell performance could be obtained as a result of the use of interdigitated fuel/air distributors. This interdigitated idea has been shown to be successful in the low temperature PEMFCs, but no attempts have been made to extend this design to SOFCs in open literature. Unlike the PEMFC, SOFC usually has a thick supporting porous electrode. By introducing strong convective term into the fuel/oxidant transport processes inside the thick SOFC porous electrode, the applicability/accuracy of simple porous media models, such as Fick’s model, must be examined. In this study, the diffusive and forced convective mass transport in a porous anode of a solid oxide fuel cell is studied with simulated electrochemical reactions along the electrode/electrolyte interface. The performance of the Fick’s model is compared with the Dust Gas Model calculation.

THE SIMULATION MODEL

The model domain is a 2-dimensional cross section of the interdigitated flow field design, shown in Figure 2. The anode thickness is set to be 0.25 mm with a height of 2 mm. Steady state simulation for an ideal gas mixture of H2-H2O was performed using FEMLAB. The process is isothermal without surface diffusion and there are no external forces. The gas mixture is treated as incompressible due to the low flow velocities. Because of the high operating temperature, the activation loss in the anode is neglected. The reaction layer, where the hydrogen is oxidized along the electrode/electrolyte interface, has zero thickness. The over-potential of the electrochemical reaction is specified on the reactive boundary.

Figure 1. Interdigitated Flow Field Design Figure 2. The Calculation Domain.
**Governing Equations**

Equation 1 is the steady state continuity equation

$$\nabla \cdot (C \times V) = 0$$  \[1\]

Where \( C \) is the total gas mixture molar concentration, \( V \) is the velocity, \( C \times V \) is the total molar flux.

For continuous gas phase flow in the porous anode, Darcy's law, Equation 2, is used.

$$V = -\frac{k_p}{\mu} \nabla P$$  \[2\]

Where, \( k_p \) is the permeability of the medium, \( \mu \) is the dynamic viscosity of the gas mixture.

At inlet and outlet, pressures are specified. Along the reaction side,

$$n \left( -\frac{k_p}{\mu R T} \nabla P \right) = \frac{I}{2F},$$

where, \( I \) is the local current density, \( 2 \) is the number of the electrons in the electrochemical reaction and \( F \) is the Faraday constant.

**Fick's Law (H\(_2\)-H\(_2\)O)**

The Diffusion Flux is calculated using equation 3.

$$N_i^d = -D_i^e C_i$$  \[3\]

\( D_i^e \) is the effective diffusivity of \( H_2 \) in the anode. By assuming equal counter-current molar fluxes, according to Chan et al. (8), the composition independent \( D_i^e \) can be found.

$$D_i^e = \left( \frac{1}{D_{i2}^e} + \frac{1}{D_{i2k}^e} \right)^{-1}$$

\( D_{i2}^e \) is the effective binary bulk diffusion coefficient for \( H_2 \) and \( H_2O \). \( D_{i2k}^e \) is the \( H_2 \) effective Knudsen diffusion coefficient, which depends on temperature and structure of the porous material.

For a convective flow in a porous medium, combining the diffusive and convective fluxes, the flux equation can be written as equation 4.

$$N_i = -(\frac{1}{D_{i2}^e} + \frac{1}{D_{i2k}^e})^{-1} \nabla C_i = \frac{X_1 k_p P}{RT \mu} \nabla P$$  \[4\]

The current density in the 2-dimensional case varies with position along the reaction boundary and is proportional to the local electrochemical reactions. For an exact treatment of this boundary, the entire cell (not just the anode) and the electrical potential distribution must be included in the calculation. In this study, the current density is related to the polarization and the boundary \( H_2 \) molar fraction using the Butler-Volmer equation:
\[ I(y) = \frac{I_0 C_i(y)}{C_{i,ref}} \exp(\frac{\alpha F}{RT} \eta) \]  

Where, \( I_0 \) is the exchange current density \((A/m^2)\); \( C_{i,ref} \) is a reference H\(_2\) molar fraction, taken to be the inlet molar fraction; \( \alpha \) is the transfer coefficient and \( \eta \) is the polarization, which is an input parameter. The calculated local molar fractions and current densities are averaged over the reaction boundary for comparisons.

**Dusty Gas Model**

Equation 6 is the general constitutive flux relation from the gas kinetic theory.

\[
\frac{N_i}{D_i} + \sum_{j \neq i} \left( \frac{C_i N_i}{D_i} - \frac{C_j N_j}{D_j} \right) = -\frac{P}{RT} \nabla X_i - \frac{C_i}{RT} \left( 1 + \frac{k_P}{\mu D_i} \right) \nabla \rho
\]

For a H\(_2\)-H\(_2\)O binary gas mixture, the H\(_2\) molar flux is given in equation 7.

\[
N_1 = -\frac{P}{RT} \left( \frac{1}{D_{2k}^e} + \frac{1}{D_{12}^e} \left( \frac{C_1}{D_{1k}^e} + \frac{C_2}{D_{2k}^e} \right) \right) \nabla C_1 - \frac{C_1}{RT} \left( \frac{1}{D_{2k}^e} + \frac{1}{D_{12}^e} \left( \frac{C_1}{D_{1k}^e} + \frac{C_2}{D_{2k}^e} \right) \right) + \frac{k_P \mu}{\rho} \nabla \rho
\]

\[ C_2 = 1 - C_1 \]

**RESULTS AND DISCUSSIONS**

The effect of fuel inlet concentration on the polarization has been studied using the Fick's law. The high concentration case has a hydrogen inlet molar concentration of 80%. The pressure at inlet was chosen to be 1.1 times the ambient pressure; the outlet pressure is the ambient pressure; the polarization is set to be 0.3V and the pore size of the porous medium is 1.5 \( \mu \)m. Using the Fick's model, the FEMLAB predicted hydrogen concentration contour is shown in Figure 3. Along the reaction boundary, the predicted hydrogen concentration is shown in Figure 4, with an averaged H\(_2\) molar fraction of 77.5%
By reducing the hydrogen concentration at inlet to 40%, with no other changes in the setting parameter, FEMLAB predicted a near linear decrease of averaged H$_2$ molar fraction along the reaction sites, with a similar pattern of mole fraction distribution, see Figure 5.

Further calculations were performed with a reduced inlet hydrogen concentration of 20% and 10%, corresponding results are shown in Figure 6. A reduction of inlet fuel molar fraction from 20% to 10% leads to a reduction of H$_2$ concentration along the reaction sites by 55%, with slight deviations from the linear relation in the high concentration region.

The discrepancies between the Fick's model and the Dusty Gas Model have been studied by changing the inlet fuel concentration, the concentration polarization or current density and the pore sizes. Two hydrogen inlet concentration cases are studied, a high value of 80% and a low value of 20%; the concentration polarization is set to be either 0.05V or 0.3V; and the mean pore sizes of the porous electrodes are 1.5 $\mu$m and 0.5 $\mu$m respectively. Under each set of condition, the hydrogen concentration and the current density along the reaction boundary is predicted using the Fick's model and the Dusty Gas Model. The pressure at the inlet was chosen to be 1.1 times the ambient pressure; the outlet pressure is the ambient pressure.

Figure 4. H$_2$ molar fraction along the reaction boundary for $C_{\text{inlet}} = 80\%$.

Figure 5. H$_2$ molar fractions along the reaction boundary for $C_{\text{inlet}} = 40\%$. 
Figure 6. Averaged H₂ concentration along the reaction boundary.

**Case 1:** Low inlet H₂ concentration of 20%, low concentration polarization of 0.05V and a large mean pore size of 1.5 μm.

|                  | Fick’s model | Dusty Gas Model |
|------------------|--------------|-----------------|
| Averaged H₂ Concentration | 0.192        | 0.195           |
| Current Density (A/m²)      | 1417         | 1428            |

The Fick’s model gives similar fuel concentration and current density along the active boundary as those predicted using the Dusty Gas Model.

**Case 2:** Low inlet H₂ concentration of 20%, high concentration polarization of 0.3V and a large mean pore size of 1.5 μm.

|                  | Fick’s model | Dusty Gas Model |
|------------------|--------------|-----------------|
| Averaged H₂ Concentration | 0.175        | 0.177           |
| Current Density (A/m²)      | 5592         | 5667            |

The difference in the fuel concentration along the active boundary and the current density between the Fick’s model and the Dusty Gas Model is about 1%. Cases 1 and 2 demonstrate that with low fuel concentration and large pore sizes, no significant differences between the Fick’s law and the Dusty Gas Model results are found, regardless of the current density. This prediction is consistent with the 1-dimensional simulations reported by Suwanwarangkul et al. (4).

**Case 3:** Low inlet H₂ concentration of 20%, high concentration polarization of 0.3V and a small mean pore size of 0.5 μm.

|                  | Fick’s model | Dusty Gas Model |
|------------------|--------------|-----------------|
| Averaged H₂ Concentration | 0.142        | 0.167           |
| Current Density (A/m²)      | 4573         | 5248            |
The difference in the averaged H$_2$ concentration along the reaction boundary predicted using the Fick’s model and the Dusty Gas Model is about 18%. The difference in the predicted current density is about 15%. This is because under a small pore diameter, the Knudsen flow is the dominant feature and Fick’s equal molar counter flow assumption is not valid in this regime.

**Case 4:** Low inlet H$_2$ concentration of 20%, small concentration polarization of 0.05V and a small mean pore size of 0.5 µm.

|                       | Fick’s model | Dusty Gas Model |
|-----------------------|--------------|-----------------|
| Averaged H$_2$ Concentration | 0.180        | 0.185           |
| Current Density (A/m$^2$)     | 1350         | 1401            |

At low current density with a small pore size and low fuel concentration, the difference in the averaged H$_2$ concentration along the reaction boundary predicted by the Fick’s law and the Dusty Gas Model is about 3%. The difference in the predicted current density is about 4%.

**Case 5:** High inlet H$_2$ concentration of 80%, small concentration polarization of 0.05V and a large mean pore size of 1.5 µm.

|                       | Fick’s model | Dusty Gas Model |
|-----------------------|--------------|-----------------|
| Averaged H$_2$ Concentration | 0.795        | 0.798           |
| Current Density (A/m$^2$)     | 1500         | 1495            |

Under high fuel concentration, low current density and large pore size, the Knudsen diffusion is negligible (bulk diffusion limit). The difference between the two models is negligible.

**Case 6:** High inlet H$_2$ concentration of 80%, high concentration polarization of 0.3V and a large mean pore size of 1.5 µm.

|                       | Fick’s model | Dusty Gas Model |
|-----------------------|--------------|-----------------|
| Averaged H$_2$ Concentration | 0.750        | 0.754           |
| Current Density (A/m$^2$)     | 6242         | 6175            |

This case is also within the bulk diffusion limit, thus very small differences between these two models were found.

**Case 7:** High inlet H$_2$ concentration of 80%, small concentration polarization of 0.05V and a small mean pore size of 0.5 µm.

|                       | Fick’s model | Dusty Gas Model |
|-----------------------|--------------|-----------------|
| Averaged H$_2$ Concentration | 0.79         | 0.795           |
| Current Density (A/m$^2$)     | 1485         | 1470            |

No significant differences were found between the results of the two models under the conditions of large fuel concentration and low current density, even for the small pore size, due to the dominance of bulk diffusion.
Case 8: High inlet H₂ concentration of 80%, large concentration polarization of 0.3V and a small mean pore size of 0.5 μm.

|                         | Fick’s model | Dusty Gas Model |
|-------------------------|--------------|-----------------|
| Averaged H₂ Concentration | 0.750        | 0.785           |
| Current Density (A/m²)   | 6078         | 6146            |

Under the condition of high current density and small pore size, the two models had a discrepancy of averaged fuel concentration along the reaction boundary of about 4.7%.

CONCLUSIONS

This paper presents the numerical simulations of gas transport in the porous electrodes of the Solid Oxide Fuel Cells with an interdigitated flow channel design using FEMLAB. Two porous media mass transport models, the Fick’s Model and the Dusty Gas Model were used in the simulations. The Fick’s model is used to study the concentration difference between the feeding channel and the fuel cell reaction boundary. Concentration along the reaction boundary is a strong linear function of the inlet gas concentration except in the low inlet concentrations region. The increase in current densities results in the increase of polarization regardless of inlet fuel concentration or the mean pore size of the porous electrode.

Simple but less accurate Fick’s model is validated against the Dusty Gas Model results. Fick’s law generally predict a higher polarization than the Dusty Gas Model results. It is found that for a combined diffusive and convective flow in the SOFC porous electrodes, when the fuel concentration is low and the pore size is small, the Knudsen diffusion plays a dominant rule, thus Fick’s model gives inaccurate results. Hence in such circumstances the Dusty Gas Model should be used.

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