DEVELOPMENT OF A NUMERICAL SOFC CATHODE MODEL

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ABSTRACT

A cathode model, suitable for incorporation into planar solid oxide fuel cell stack performance models, has been developed. Mechanisms considered in the formulation include mass transfer from the gas channel to the electrode surface, gaseous (bulk and pore) diffusion through the porous electrode, adsorption of oxygen onto active sites at the cathode/electrolyte interface, and electrochemical reduction of the adsorbed oxygen. The reaction step is assumed to be rate limiting with the adsorption step in equilibrium. Fick’s law is used to model the diffusion step with the adsorption step represented by a n-site Langmuir adsorption isotherm. The Butler-Volmer equation is used to describe the charge transfer process. Model parameters have been determined by optimisation against published data. For co-flow arrangements, performance of the cell near the fuel inlet is limited by diffusion.

INTRODUCTION

Behaviour prediction through numerical simulation of solid oxide fuel cells (SOFC) is a cost-effective means of generating design data. However, confidence in the simulated result depends on the accuracy of the input data and the physical rigour of the mathematical formulation. In general, modelling of SOFC stacks is far more advanced than modelling of micro-phenomena, like the electrode reactions, on which the stack models are built. Improved mathematical formulations describing the electrode performance are required to increase the certainty in the simulation results.

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Generally, electrode behavior is incorporated into fuel cell model through a simple potential balance.

\[ E = E_0 - \eta - \eta_{IR} \]  \hspace{1cm} [1]

where \( E \) is the operating voltage and \( E_0 \) is the Nernst equilibrium potential. \( \eta \) is a lumped term containing all the voltage losses, except the resistive losses, which are treated separately. Common approaches to calculate \( \eta \) include assuming it to be a constant (1) or assuming a resistive-type relation with the temperature (2). These approaches offer rapid implementation of electrode models into stack models but bear little resemblance to the physical picture.

In general, the lumped \( \eta \) can be split into a number of terms.

\[ \eta = \eta_{df,c} + \eta_{df,a} + \eta_{kin,c} + \eta_{kin,a} \]  \hspace{1cm} [2]

Sub-models for all these terms need to be developed. The first two terms are due to in-plane diffusion (3) and have not been widely combined with electrode kinetics. Some basic work on more detailed kinetics, to calculate the last two terms, has been presented (4) but not incorporated into stack models.

The aim of this paper is to present an integrated cathode model coupling fluid film mass transfer and diffusion in the electrode with adsorption and reaction phenomena at the electrode/electrolyte interface. Model predictions for a co-flow SOFC using the cathode model are also presented.

MODEL DEVELOPMENT

Planar SOFC's consist of individual cells linked in series to form stacks. The individual cells are separated, but electrically connected, by a bi-polar or interconnect plate. The interconnect features channels for gas distribution and webs for current collection. From a modelling perspective, a physical and mathematical description of the transport of \( O_2 \) from the gas in the channels to the cathode/electrolyte interface is required.

Physical and Mathematical Description

Transport of \( O_2 \) from the air channels to the cathode/electrolyte interface is achieved in a number of steps. Initially, \( O_2 \) molecules diffuse from the bulk phase to the electrode surface through an external fluid film established as a result of the laminar flow conditions.
Reynolds numbers are typically 100 for the cathode channels. O₂ then diffuses through the porous cathode structure to the electrolyte surface. Comparing the mean free path of the gas molecules with the pore structure of the cathode suggests that the transport mechanism is a combination of pore and Knudsen diffusion (5). The diffusion problem is strictly two-dimensional. However, cross-plane diffusion has been shown to be negligible (6) compared to in-plane diffusion—a consequence of the planar geometry where the current collection webs shield the electrode surfaces from the bulk convective flow.

The differential equation describing the in-plane diffusion of O₂ underneath the current collection web having thickness T_w is

\[ D_{\text{eff},O_2} \frac{P}{R_g T_e} \frac{d^2 X_{O_2}}{dy^2} = \frac{j(y)}{4F_{\text{e}}} \quad [3] \]

where P is the total pressure of the system, \( X_{O_2} \) is the mole fraction of O₂ in the porous cathode, and y is the co-ordinate of the current collection webbing perpendicular to the stacking direction. \( D_{\text{eff},O_2} \) is the effective diffusivity of O₂ in N₂. The above equation is solved with the following boundary conditions,

\[ y = 0; \quad \frac{dX_{O_2}}{dy} = 0 \quad [4] \]

\[ y = \frac{T_w}{2}; \quad D_{\text{eff},O_2} \frac{dX_{O_2}}{dy} = k_{m,O_2}(X_{O_2,b} - X_{O_2}) \quad [5] \]

The boundary condition at \( y = T_w/2 \) is based on the assumption that the in-plane diffusion is balanced by the laminar film mass transfer. The film mass transfer coefficient, \( k_{m,O_2} \) is estimated by taking the Sherwood number to be 4.5, corresponding to fully developed laminar flow in the channels (8). The effective diffusion coefficient \( D_{\text{eff},O_2} \) is calculated using the procedure outlined in (5). The ratio of porosity to tortuosity is assumed to be 0.1 (6). A pore radius of 1 µm is assumed.

Following (7), from the concentration distribution of O₂, the associated cathodic diffusion overpotential can then be evaluated from:

\[ \eta_{\text{diff},c}(y) = - \frac{R T_e}{n F} \ln \left( \frac{X_{O_2}(y)}{X_{O_2,b}} \right) \quad [6] \]
Upon arrival at the electrolyte surface, O\textsubscript{2} is reduced to oxide ions through reactions with electrons. The detailed mechanism for this process is unclear. However, a two step process has been suggested for O\textsubscript{2} reduction on Platinum (9). The mechanism consists of O\textsubscript{2} adsorption,

\[ \text{O}_2 \text{(gas)} + 2.\text{S} \leftrightarrow \text{O}_2 \text{(ads)} \]  

followed by charge transfer,

\[ \text{O}_2 \text{(ads)} + 4.\text{e}^{-} \leftrightarrow 2\text{ O}^{2-} \]  

In the literature, it has been suggested that the surface diffusion of adsorbed O\textsubscript{2} may also play an important role (4). However, in this study, surface diffusion is ignored as its inclusion would involve additional unknown parameters which need to be determined from experimental data. For the purpose of the model development, the adsorption step is assumed to be in equilibrium and the charge transfer step is a rate limiting.

In (9), the adsorption process has been modelled by a 2-site Langmuir isotherm. However, fitting their model to the experimental data on LSM material yielded a poor correlation. Hence, in this work, the adsorption step is described by a n-site Langmuir isotherm (10). The n-site adsorption isotherm assumes that n vacant active sites are needed to adsorb one O\textsubscript{2} molecule.

\[ \text{O}_2 \text{(gas)} + n.\text{S} \leftrightarrow n\text{O}_2 \text{(ads)} \]  

The fractional surface coverage of the adsorbed O\textsubscript{2} can be written as,

\[ \theta = \frac{(b.P.X_{O_2})^{1/a}}{1 + (b.P.X_{O_2})^{1/a}} \]  

The parameter b, the Langmuir equilibrium constant, is a function of temperature and is described by the van't Hoff equation (10),

\[ b = b_0 \exp \left( \frac{\Delta H}{R.T} \right) \]  

in which b\textsubscript{0} is the frequency factor and \(\Delta H\) is the heat of adsorption. Since adsorption is an exothermic process, \(\Delta H\) should be positive.

The parameter n, number of active sites, is allowed to vary with temperature according to,

\[ \frac{1}{n} = \alpha_1 + \frac{\alpha_2}{T} \]  

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The charge transfer process at the cathode is modelled by the Butler-Volmer equation (11),

\[ j = j_{0,c} \left[ \exp \left( \frac{\alpha_c \eta_{kin,c} F}{R \cdot T_s} \right) - \exp \left( - \frac{\alpha_{\alpha} \eta_{kin,c} F}{R \cdot T_s} \right) \right] \]  

where \( j_{0,c} \) is the exchange current density. \( \eta_{kin,c} \) is the resulting cathodic overpotential due to a net flow of electrons when the cell is subjected to a current density \( j \).

The constants \( \alpha_c \) and \( \alpha_{\alpha} \) are charge transfer coefficients which can be determined by fitting the Butler-Volmer equation to the experimental data at low and high cathodic overpotentials respectively (12). In this work, their values are assumed to be unity. Following (9), the charge transfer step is assumed to be proportional to the adsorbed \( O_2 \) concentration. Then the exchange current density is given by:

\[ j_{0,c} = 4FK_{kin,c} [\theta (1 - \theta)]^{1/2} \]  

where \( K_{kin,c} \) is the kinetic reduction rate constant, while \( \theta \) is the fractional surface coverage of the cathode-electrolyte interface by the adsorbed \( O_2 \).

The dependency of \( O_2 \) reduction process on temperature is assumed to follow the Arrhenius form and the rate constant \( K_{kin,c} \) is given by,

\[ K_{kin,c} = K_{kin,co} \exp \left( - \frac{E_{act,c}}{R \cdot T_s} \right) \]  

in which \( K_{kin,co} \) and \( E_{act,c} \) are the frequency factor and activation energy of the reaction respectively.

Essentially, the cathode reaction kinetics depend on the following six parameters \( K_{kin,c}, E_{act,c}, b_0, \Delta H, \alpha_1 \) and \( \alpha_2 \) which can be estimated from the current density versus overpotential data at different temperatures and partial pressures.

PARAMETER ESTIMATION

The parameters in the proposed model were estimated using the experimental data reported in the literature (13,14). In (13), overpotential versus current density data at an \( O_2 \) partial pressure of 0.21 atm and at three different temperatures has been reported. In (14), overpotential versus current data as a function of temperature and at different \( O_2 \) partial pressures is available.
The Butler-Volmer equation was fitted to the experimental data from (13) to obtain the $j_{0,c}$ values at the three temperatures. To account for the dependency on O$_2$ partial pressure, these exchange current densities are then combined with the data from (14) to obtain overpotential versus current density data at different O$_2$ partial pressures.

The model parameters are then estimated by fitting to this data using a non-linear regression based on Marquardt modified steepest descent technique which minimises the sum of the squares of the relative errors. Figure 1 shows the fits for exchange current density versus oxygen partial pressures at three temperatures 800°C, 900°C and 1000°C. A good correlation between the model and the data is evident.

RESULTS AND DISCUSSION

Simulations were performed to assess the effect of the proposed model on the performance predictions for a co-flow SOFC. Completely reformed natural gas at 850°C and air at 800°C are taken as the fuel and oxidant respectively. The anode kinetics is assumed to be described by the expression reported in the literature (15). The in-plane diffusion equations are transformed into algebraic equations using the orthogonal collocation technique (16) and coupled with the electrochemical kinetic equations. The resulting set of non-linear algebraic equations is solved by a fast Quasi-Newton method.

Typical profiles of gas phase oxygen concentration in the cathode and current density along the channel length obtained from the simulations are shown in Figures 2 and 3. The figures clearly demonstrate that under the current collection webs, where in-plane diffusion is important, O$_2$ concentration and current density are significantly lower than the values for the free stream conditions in the channel.

From these figures, following observations can be made. The gas phase O$_2$ concentration in the cathode is less than 0.21 (even at the inlet) due to the laminar boundary layer. Near the inlet, due to the presence of H$_2$ rich fuel, the extent of the electrode reaction and hence the current density is quite high and O$_2$ concentration under the webs approaches zero. i.e., diffusion is limiting the performance. Near the outlet, although O$_2$ concentration is high, because of the low H$_2$ and high H$_2$O concentrations, the extent of electrode reaction is low which results in lower current density and the performance is less likely to be limited by diffusion.
CONCLUSION

In this paper, a kinetic description based on adsorption and charge transfer has been presented to describe O₂ electrochemical reduction in SOFC's. The kinetic model is coupled with film mass transfer and in-plane diffusion to build a comprehensive cathode model. Stack simulations show the importance of in-plane diffusion and significant variation in current density and O₂ partial pressures under the current collection webs in planar SOFC's.

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![Graph](image-url)

**Figure 1:** Comparison of model predictions and experimental data (13,14).
Figure 2: Typical gas phase $O_2$ concentration profiles in the air electrode.

Figure 3: Typical current density profiles in a SOFC in the co-flow configuration.