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Three-Dimensional CFD Modelling of PEM Fuel Cells

An Investigation into the Effects of Water Flooding

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Abstract

In this work, a three-dimensional PEM fuel cell model has been developed and is used to investigate the effects of water flooding on cell performance parameters. The presence of liquid water in the cathode gas diffusion layer (GDL) limits the flow of reactants to the cathode catalyst layer, thereby reducing the overall reaction rate and curtailing the maximum power that can be derived from the cell. To characterize the effects of water flooding on gas diffusion, effective diffusivity models that account for the tortuosity and relative water saturation of the porous fuel cell electrodes have been derived from percolation theory and coupled with the CFD model within a single phase flow skeleton. The governing equations of the overall three-dimensional PEM fuel cell model, which are a representative of the coupled CFD and percolation theory based effective diffusivity models, are then solved using the finite volume method. Parametric studies have been conducted to characterize the effects of gas diffusion layer permeability, inlet humidity and diffusivity of the reactants on the various cell performance parameters such as concentration of reactants/products and cell current densities. It is determined that the gas diffusion layer permeability has little or no effect on the current densities due to the diffusion dominated nature of the gas flow. However, through the incorporation of percolation theory based effective diffusivity model; a marked reduction in the cell performance is observed which closely resembles published experimental observations. This is a reasonable approximation for effects of water flooding which has been inherently used for further parametric studies.

Keywords: PEM fuel cells, Percolation theory, Electrochemistry, Fluid mechanics, Porous media.

1. Introduction

Proton exchange membrane (PEM) fuel cells with hydrogen as the fuel are envisioned to be the next generation environmental friendly energy alternatives (Hirschenhofer, 1994; Fontes & Nilsson, 2001) as they have promising applications in the automotive and power sector due to factors such as low operating temperatures with zero/low emissions, a modular structure, quick start-up times, high power density and corrosion resistance (Larminie & Dicks, 2000). Hence, efforts targeted towards gaining an in-depth understanding of the dominant multi-physics within a fuel cell can aid in making them commercially viable and providing the desired power output/energy gains. Computational fuel cell models prove to be a valuable tool for engineers as they help in undertaking reliable simulations, and design optimization studies, facilitate the introduction of cheaper materials/fabrication techniques and provide cost/time effective solutions to appraise the design of complicated cell configurations. However, to date there have been no complete and generic computational PEM fuel cell models (Biyikoglu, 2005) that can account for all the complexities associated with the underlying multi-physics in a single mathematical framework.

The performance of a PEM fuel cell depends markedly on the water content (Sousa Jr. *et al.*, 2005) within the polymer membrane. Dehydration of the cell affects the proton resistance of the polymer membrane and electrolyte in the cathode catalyst layer and can reduce performance due to an increase in the voltage across the membrane (Larminie & Dicks, 2000; Yi *et al.*, 2004). To avoid dehydration of the polymer electrolyte, the inlet flows of reactants are often injected mixed with water vapour. However, with excess water production and low diffusion flux (reducing the rate of water-disposal), condensation may occur in the cathode porous layer, clogging the pores and blocking the transport of species to the reaction sites. For these reasons, water management within a PEMFC is a critical issue (Mazumder & Cole, 2003 a&b), especially during prolonged periods of operation.

Despite this, the majority of CFD models for PEM fuel cells either do not consider the effects of liquid-water flooding on cell performance or use simplistic assumptions. In the last decade or so there have been various analytical, semi-empirical, one-dimensional and two-dimensional PEMFC models that have been proposed by Bernardi *et al.*(1990, 1992), Springer *et al.*(1991), Fuller & Newman (1993), Nyugen *et al.*(1993), Amphlett *et al.*(1995), Standaert *et al.*(1996,1998), Bevers *et al.*(1997), Hubertus *et al.*(1998), Gurau *et al.*(1998), Yi *et al.*(1998), Eikerling *et al.*(1998), Wohr *et al.*(1998), Singh *et al.*(1999), Scott *et al.*(2000), Squadrito *et al.*(1999), Baschuk *et al.*(2000), Dannenberg *et al.*(2000), Hsing *et al.*(2000), Um *et al.*(2000), Rowe *et al.* (2001), Maggio *et*

al.(2001), Wang *et al.*(2001), Eaton *et al.*(2001), Chan *et al.*(2003), Natarajan *et al.*(2003), Maxoulis *et al.*(2004) and Siegel *et al.*(2004).

The earliest models by Bernardi *et al.*(1990, 1992), Springer *et al.*(1991) and Nyugen *et al.*(1993) were semi-empirical in nature; based on membrane experimental data used for the calibration of curves. More advanced two-dimensional modelling studies can be attributed to Wang *et al.* (2001). They studied the effects of two-phase flow and transport of reactant gases within the cathode by applying a multiphase mixing model. Single and two-phase transport regimes were discussed and developed analytically (one-dimensionally), allowing simple quantification of the two separate regimes. They simulated the transition between the water phases occurring at a threshold current density value which corresponds to the first appearance of liquid water at the interface between the membrane and the cathode. Despite the model being fairly comprehensive, their studies were limited to cathode zone simulations; as a result it is unclear as to how well the model would cope with full PEMFC simulations.

Later, You & Liu (2006) developed a 2-D, two-phase multi-component mixture model to describe the two-phase flow field in the flow channel and the GDL. This model was based on a multi-component mixture model proposed by Wang & Cheng (1997)., The study considered the effects of two-phase flow on convection/diffusion and species transport. Polarization curves under different cathode pressures were simulated and validated against the experimental studies conducted by Huang (2000). They concluded that with an increase of the cathode pressure, both the oxygen molar concentration and exchange current density increase resulting in enhanced fuel cell output voltage for a given over-potential.

Analytical, semi-empirical, 1-D and 2-D modeling studies are sufficient for predicting cell performance in the rate limited regimes, however, when mass transport limitations arise they tend to be highly inadequate as the effects of cell geometrical configurations on mass transport are not accounted for. Hence, in the context of design optimization efforts that would make PEM fuel cells commercially feasible, 3-D CFD modeling studies are imperative as they help in gaining better understanding of the realistic physical phenomena associated with the bulk flow in the gas channels and the orthogonal flow within the electrodes and parallel to the membrane.

Dutta *et al.* (2000, 2001) developed a 3-D fuel cell model.. The developed models were capable of solving for species concentrations along the gas channels and current density over the membrane surface. This model was configured to match a number of different flow cases from the work of Yi *et al.*(1998) and Fuller *et al.* (1993) investigating dry oxygen and humidified air cases and co-flow/counter-flow cases. The effect of porosity on the

diffusion coefficient was accounted for by arbitrarily decreasing the binary diffusion coefficients by 50% rather than using a more comprehensive Bruggeman correlation. Linear extrapolation was used to allow grid independence by interpolating species concentrations on the catalyst layer surfaces. The model was used to investigate two-dimensional current density distributions, which is only possible with a three dimensional model, and the width-averaged current density distributions across the membrane.

Mazumder *et al.* (2003a) presented a rigorous 3-D model for PEM fuel cells with no liquid water transport present. Later, (Mazumder *et al.* (2003b)) extended this PEMFC model, predicting water transport effects on cell performance. The resultant model could qualitatively predict the effects of water flooding, however, due to a lack of data for electro-osmotic drag and capillary diffusion coefficients, the numerical predictions still over-predicted the experimental polarization curves at high current densities.. The capillary diffusion co-efficient models used correspond to the ones used by Wang *et al.* (2001), however, the numerical values used still remain uncertain. Phase change effects associated with water vapour condensation were tackled by assuming equilibrium phase transformations. This assumption is reasonable as a comprehensive two-phase flow analysis makes the PEMFC model computationally expensive. While the idea was generally sound, the scaling factors they considered in their simulations are still questionable. Key results from their studies indicate that 3-D simulations through inclusion of clogging effects are imperative to accurately capture the localised water saturation levels and cell voltage-current characteristics in comparison to 2-D modelling.

Um & Wang (2004) presented a 3-D CFD model including gas channels and MEA similar to that of Dutta *et al.* (2000, 2001). A single domain model features a detailed MEA water transport model which was used to compare two different flow-fields, namely straight and inter-digitated patterns. Their model shows that forced convection created by the use of inter-digitated flow-fields, (through the use of a positive pressure gradient) improves the flow of oxygen to the cathode catalyst layer and improves the removal of water enhancing the overall performance of the cell.

Nguyen *et al.* (2004) modelled a PEMFC under a single-phase flow assumption, and considered a serpentine flow field (modelling a repetitive unit of the serpentine channel). Diffusion in the porous zones was computed using the Stefan-Maxwell equation and the Bruggeman correlation. The membrane was considered to be fully humidified. A unique feature of the model was to use an electrical voltage-to-current algorithm that computes the local over potential by solving for the potential field. The results are significantly different from cases where a constant surface

over potential is assumed. As with all single-phase models there was significant discrepancy found between the model and experimental results at high current densities due to the effects of water flooding.

Lum *et al.* (2005) presented a steady-state, three dimensional, isothermal model of a full PEM fuel cell, similar to that of Dutta *et al.* (2000). The model was single-phase, only considering the vapour phase of water. This model was validated both globally and locally at points along the gas channel using experimental data from a segmented fuel cell. A deviation from experimental results was found at high current density/high humidity due to liquid water flooding. However, at a lower humidity/current density, excellent agreement with the experimental data was observed. It was found that there was a limiting permeability below which very little performance deterioration will occur as in the gas diffusion layers the flow is diffusion dominated, which has also been observed in this study. This is not observed experimentally. In practice permeability will have a marked effect as liquid water will directly affect the reactant flow rates and result in a significant performance drop, especially in fuel cells facilitated by forced convection such as inter-digitated flow-fields.

Sivertsen & Dijali (2005) developed a 3-D single phase, non-isothermal PEMFC computer model, accounting for distributed overpotential at the cathode catalyst layer and heat sources at each electrode, also incorporating, heat transfer in the solids and gases. Mass transport was described by the Stefan-Maxwell equations by calculating binary diffusion coefficients. To account for additional drag caused by the irregular shape and length pore scales, an effective diffusion coefficient was used in the simulations, which assumes a constant tortuosity factor of 3. The water transport phenomenon was based on the model proposed by Janssen (2001). The studies show that changing the conductivity radically alters the current density.

Jiao *et al.* (2006) simulated 3-D straight micro-parallel-channels with inlet and outlet manifolds for a PEM fuel cell stack using a volume of fluid (VOF), two-phase flow model under different initial water concentrations. The effects of surface tension and wall-adhesion were modelled using the continuum surface force (CSF) model proposed by Brackbill *et al.* (1992). Their parametric studies resulted in numerous design recommendations related to alleviating the water flooding problem, such as, proposition of serpentine gas-flow channels, inlet/outlet manifolds with reduced/increased cross-sectional area respectively, curved wall facing the air flow inlet and selection of materials with less water adhesion effects.

Although most of the recent 3-D modelling studies are fairly comprehensive, the majority directly concern issues related to either flow-optimization, natural convection on the cathode side, or to the comparison of straight

and inter-digitated flow-fields, ignoring the effects arising from multi-physics and coupled flow/mass-transport in the process. The remainder of the 3-D PEMFC studies that considering water-flooding are either based on simplistic treatments such as arbitrarily altering the conductivity/binary diffusivities, neglecting changes in porosity/permeability, assuming no interaction between phases in sub-domains or including artificial parameters in water transport models which cannot be determined experimentally. The attempt of this work is to focus on such simplistic assumptions and re-consider the use of diffusivity models derived from the percolation theory, that are computationally inexpensive, to investigate the effects of water flooding.

Selyacov *et al.* (1996) gave an overview of the application of percolation theory to the modelling of transport in porous media. Analytical methods for determining conductivity parameters, such as electrical conductivity and permeability were presented. These methods are derived using microscopic flow models and percolation relationships, considering single and multiphase flows. Pharoah *et al.* (2006) later reviewed the approaches adopted to model the effective transport coefficients, chemical species diffusivity, electrical conductivity, thermal conductivity and the hydraulic permeability of carbon-fibre based porous electrodes in PEM fuel cells.

Nam & Kaviany (2003) were the first to study in detail the effects of the formation/distribution of condensed water in PEM fuel cell diffusion medium on cell performance by a reduction in effective mass diffusivity. A local mass-diffusivity model of a fibrous diffusion medium was developed as a function of the local porosity and water saturation, using a computational network-model, considering the structure of the GDL as stacks of randomly shifted grids with constant pore size, for species diffusion.. Diffusion was then solved over a cubic grid considering face and edge diffusion between connected cells.. Close agreements were obtained against the results of Tomadakis *et al.* (1993). The mass diffusivity model was then used in conjunction with the capillary hydrodynamics, two-phase flow behaviour, water formation rate and the condensation kinetics to determine the 1-D distribution of water saturation. Tseng *et al.* (2005) performed numerous experiments to study the structure effects of gas diffusion layer (GDL) and microporous layer (MPL) characteristics on the water management/performance of a PEM fuel cell. The pore-size range, pore-size distribution, pore-structure, surface contact angle, electric contact resistance and internal structure (i.e. pore-size distribution and gas-permeability) were determined, using scanning electron microscopy (SEM), porosimetry, and a surface contact angle meter, to investigate their effects on cell performance.. Finally they investigated the effects of MPL, thickness of MPL, PTFE loadings and the type of carbon black used in MPL on the cell performance.

In the current study, the effects of liquid water-flooding are investigated by considering a single-phase 3-D PEM fuel cell model, (similar to models developed by Springer *et al.* (1991), Dutta *et al.* (2000) and Lum *et al.* (2005) amongst others) in conjunction with effective diffusivity models derived from percolation theory based on the works of Selyacov *et al.* (1996), Nam *et al.* (2000) and Tseng *et al.* (2005). This work's parametric studies focus on simulating design parameters of interest such as average current density and its dependence on water-flooding which are related to the effective diffusivity variations. The investigations are based on a repeating section of gas channels, gas diffusion layers, catalyst layers and membrane.

The single phase assumption proves to be a computationally economic alternative in comparison to the costly two-phase flow simulations. The liquid water saturations for use in the water-flooding model are predicted using the relative-humidity values and water-vapour volume fractions, instead of the method suggested by Um and Wang (2004). Results from our model have been validated against the experimental and computational data of Shimpalee *et al.* (1999) and Lum *et al.* (2005).

2. Mathematical statement of the problem

The 3-D numerical model consists of two gas channels transporting hydrogen and oxygen reactants and water vapour (the product) mixed in air (nitrogen) to and from two porous gas diffusion layers (GDLs). The GDLs in turn transport the gases to and from the catalyst layers where all the electrochemical reactions occur. The catalyst layers sandwich a membrane through which protons and water are transported. The governing equations for the gas channels, GDLs and catalyst layers consist of continuity, conservation of momentum and species transport. Source terms are applied at the catalyst layers to represent the electrochemistry and transport through the membrane. In order to model these source terms the local current density (used to determine reaction rates) and net water transport coefficient (used to determine transport across the membrane) are calculated using auxiliary models which have been linked to the main flow solver through UDFs (User Defined Functions).

The liquid phase of water is not directly modelled. This simplification significantly reduces the complexity of the simulation; removing the need to model phase changes and allowing for an isothermal steady state simulation which is a valid assumption for low-temperature PEMFC applications.

2.1 Governing Equations

The Navier-Stokes equations, consisting of the momentum equations (eqn. 1), the continuity equation (eqn. 3) and species transport (eqn. 6) were used to model the flow of the four modelled species (under the assumption of

laminar flow and steady state) in the in the gas channels, GDLs and catalyst layers. The porous nature of the GDLs and catalyst layers was accounted for by the addition of a Darcy's law term to the momentum equations to represent the momentum associated with the surface forces in these porous zones. In this study the porous structures are assumed to be isotropic.

Fick's Law of diffusion (Bird *et al.*, 1960) was used to account for multi-component mass transport in the gas diffusion layers. In anode only two species namely hydrogen and water vapour are present whereas in cathode oxygen, nitrogen and water vapour are dominant. Although Fick's law ignores the species-species interactions, in this study we have considered each species diffusing within an approximate carrier fluid which tends to reduce this limitation. This assumption is further proven to be reasonable, as can be seen from figure 3, where the current densities predicted by Lum *et al.* (2004) who used Stephan-Maxwell multi-component diffusion, and our model are nearly identical. In addition, the species transported within the fuel cell are relatively dilute (Gallart, 2007), which further justifies the use of Fick's Law in this particular study. This in effect leads to a slight overestimation of species diffusivity. The binary (oxygen, hydrogen or water vapour in air) diffusivity coefficients are calculated using the mass fractions, pressure, temperature, critical temperature and the critical pressures of the two components (eqn. 11) based upon the works of Slattery *et al.* (1958). The governing equations and source terms are shown below in table 1.

Table 1

The catalyst layer reactions and species transport across the membrane were added to the Navier Stokes equations as volumetric source terms to the continuity equation (S_m) and species transport equations (S_k). These source terms are defined as zero in all regions except the catalyst layers and represent the consumption of hydrogen at the anode (S_{H_2}), the consumption of oxygen at the cathode (S_{O_2}), the production and flux (due to electro-osmotic drag and back diffusion) of water at the cathode (S_{cw}) and the flux of water (due to electro-osmotic drag and back diffusion) at the anode (S_{aw}). In the continuity equations the source terms for all species are summed, whereas in the species continuity equation each is applied to its own species transport equation.

The source terms in relation to the current density $I(x,y)$ and the net water transport coefficient $\alpha(x,y)$ are shown in table 2. The current density and net water transport coefficient are determined using the auxiliary equations discussed in the subsequent section.

Table 2

2.2 Auxiliary model equations

The auxiliary equations model the electrochemical reactions and determine the net water transport coefficient and local current density, and in turn volumetric source terms. These equations are provided in table 2. The empirical equations used in this work are based on Nafion 117, and can be referred to in works by Springer et al. (1993). A concise description of the auxiliary models is given below, a more detailed account can be found in Lum *et al.* (2005) and Dutta *et al.* (2000)) amongst others.

The net water transport coefficient (eqn. 12) is used to determine the transport of water vapour across the membrane and relates the relative magnitudes of back-diffusion from the cathode to the anode and the electro-osmotic drag. It is determined using the electro-osmotic drag coefficient (eqn. 20) and the water diffusion coefficient (eqn. 21). The electro-osmotic drag coefficient (eqn. 20) is an empirical relationship based on the water activity (eqn. 18) which is in turn affected by the saturation vapour pressure (eqn. 19) which is modelled empirically and referred in the work of Weast et al. (1981). The water diffusion coefficient depends on the electro-osmotic drag coefficient, the temperature, water concentration (eqns. 16-7) at the anode and cathode (which depend on the water activity), the dry mass and density of the membrane and the local current density.

The local current density (eqn. 13) defines the proton flux across the membrane, and hence the proton flux associated with each reaction which in turn defines the reaction rate. The local current density depends on the membrane conductivity, which is modelled using an empirical relationship (eqn. 15) which relates it to the membrane dry mass, dry density and water concentration and assumes no swelling of the membrane. The local current density also depends on the membrane thickness, open circuit and cell voltages and the reaction overpotential. The reaction overpotential is modelled using the Tafel equation (eqn. 14) (Tafel *et al.*, 1905) which in turn depends on the partial pressure of oxygen, the temperature, the cell voltages, the exchange current density and the local current density. Due to this implicit relationship between the current density and overpotential, these two equations are solved iteratively using the Secant method (which is employed because of its stable nature). This work neglects the contribution of the anode reaction to the cell overpotential as the exchange current density is an order of magnitude smaller.

The empirical relations and data fits used in this study have proved sufficient for many previous studies (Lum *et al.* (2005), Dutta *et al.* (2000)), and so are deemed sufficient in this work.

The diffusivity of each species is altered using a percolation-type diffusivity model. It is further assumed that each species is present in a carrier fluid i.e. air in this case and hence the equation is used to calculate the diffusivity of each species in air.

2.3 Effective Diffusivity model

The effective diffusivity model accounts for the effects of water-saturation and porosity by multiplying the Fickian diffusion coefficients for each species by scaling functions of water saturation and porosity (eqn. 22) before use the species transport equations (eqns. 6). Mathematically this can be written as

$$D_{eff} = D f(\varepsilon)g(S) \quad [22]$$

The gas diffusion layer (GDL) is typically made out of carbon-cloth in the form of a high porosity overlapping fibre structure. The effective diffusivity in such a medium can be related to the electrical conductivity by the Nernst-Einstein equation (Garboczi *et al.* (1992)).

The GDL electrical conductivity obeys simple scaling laws. Therefore the correlation length and the number of parallel conducting bonds per unit cross-sectional area in the GDL can be determined as a function of the bond occupation probability P_b and the percolation threshold P_{bc} using the following equations

$$\xi \propto (P_b - P_{bc})^{-\nu} \quad [23]$$

$$n = \frac{1}{\xi^2} \quad [24]$$

Where ξ is the correlation length, n is the number of parallel conducting bonds per unit cross sectional area, ν is the critical exponent and P_b and P_{bc} are the bond occupation probability and percolation threshold respectively.

As the conductivity is proportional to the number of parallel conducting bonds per unit cross-sectional area, by using equations 23 and 24 the scaling laws for the effective diffusivity can be determined, using equation 25

$$\frac{\lambda_1}{\lambda_0} = \frac{D_1}{D_0} = \frac{(P - P_{bc})^{2\nu}}{(1 - P_{bc})^{2\nu}} \quad [25]$$

Where ν is the correlation index, depending on the dimension of the problem only, λ_1 and λ_0 are conductivities and D_1 and D_0 are diffusivities corresponding to the current state and the percolation threshold. This equation (25) compares very favourably to the work of Tomadakis *et al.* (1993).

The value of the correlation index and percolation threshold used for the 3-D problem in this work is listed in Table 3. The bond occupation probability is the conducting fraction of the medium to the phase under consideration; in the case of the reactant gases this fraction is proportional to the porosity and inversely proportional to the saturation.

$$f(\epsilon) = \frac{(\epsilon - P_{bc})^{2v}}{(1 - P_{bc})^{2v}}, \quad g(S) = \frac{((1 - S) - P_{bc})^{2v}}{(1 - P_{bc})^{2v}} \quad [26]$$

In order to model the effective diffusivity, the saturation within each cell volume must be calculated. The relative humidity is defined by equation 27.

$$\text{Relative humidity} = \frac{P_{H_2O}}{P_w^{sat}} \quad [27]$$

Where P_{H_2O} is the partial pressure of water vapour, and P_w^{sat} is the vapour saturation pressure. In this work it is assumed that if the relative humidity in a control volume is higher than 100% the saturation is defined as the ratio of the volume of water vapour within each computational cell to the total volume of each computational cell, otherwise the saturation is zero.

$$\begin{aligned} \text{Saturation} &= \frac{\text{vol}_{H_2O}}{\text{vol}_{\text{total}}}, \text{ if relative humidity} \geq 100\% \\ \text{Saturation} &= 0, \text{ if relative humidity} < 100\% \end{aligned} \quad [28]$$

Common approximations to the effects of saturation and diffusivity are also considered (namely the Bruggeman coefficient (eqn. 29) and a power law (eqn. 30)) and compared to the use of the analytical model from percolation theory. Both diffusivity models are in the same form as equation 30.

$$f(\epsilon) = \epsilon^{1.5} \quad [29]$$

$$g(S) = (1 - S)^2 \quad [30]$$

Model 2 is derived using percolation theory and the Nernst-Einstein equation described previously. This model can be mathematically represented as equations 2.33 and 2.34.

$$f(\epsilon) = \frac{(\epsilon - 0.11)^{0.9}}{(1 - 0.11)^{0.9}} \quad [33]$$

$$g(S) = \frac{((1-S)-0.11)^{0.9}}{(1-0.11)^{0.9}} \quad [34]$$

Further details of the flooding models can be found in Dawes (2007) and Dawes *et al.* (2008).

3. Computational Results and Discussions

The governing equations were solved alongside the auxiliary equations using a finite-volume method based on a SIMPLE algorithm (Ferziger *et al.* (2002)). The source terms to model the reactions, the percolation based diffusivity model and the electrochemistry algorithm were written into ANSI C++ User-Defined-Functions (UDFs) which were then interpreted by the main CFD flow-solver FLUENT. A segregated solver was then employed to solve the final coupled set of equations.

A diagram of the solution procedure, showing an overview of the main algorithm and the points at which the sub-algorithms are incorporated is shown in figure 1.

Figure 1

In order to simplify the validation process, the geometry used in this study is identical to that studied by Dutta *et al.* (2000). The geometry represents the thin central portion of a fuel cell, one single channel wide. The computational domain does not extend through the membrane, where water and proton transport is handled using the auxiliary equations.

3.1 Computational model

The source terms are applied to the catalyst layers. These volumetric source terms model the destruction of hydrogen and oxygen, the transport of protons and the transport and creation of liquid water.

At the inlets of the computational domain Dirichlet velocity boundary conditions are applied. At the electrodes outlets, zero velocity gradient ($\nabla u = 0$) and zero species gradient ($\nabla X_k = 0$) boundary conditions are applied. These boundary conditions make the assumption that the flow is fully developed in the gas channels. This assumption is valid since the length of the gas channels is large in comparison to the width of the porous electrodes combined with the membrane. As this model represents a central strip of a much wider fuel cell, a symmetry boundary condition is applied on the top and bottom surfaces of the porous region. A no-slip condition (Ferziger (2002)) is applied to the external walls.

Table 3a

Table 3b

Table 3a and b list the prescribed boundary condition values (velocities and species concentrations) used for each humidity condition, and the physical parameters respectively.

Grid and scheme independence checks were undertaken; it was found that the solution was grid independent for the mesh shown in Figure 4, which contains a total of 14114 hexahedral cells. A scheme independence test found close correlation between the second order upwinding and QUICK schemes, but a large discrepancy with first order upwinding due to the additional artificial diffusion. For this reason second order upwinding was adopted as it proved as accurate as the higher order scheme and reduced computational expense.

Figure 2 schematically shows the dimensions of the geometry, the applied boundary conditions and the numerical grid used in this study. Due to the high aspect ratio of this geometry, in all figures the dimensions in the x and y directions are shown scaled up relative to dimensions in the z direction for clarity.

Figure 2

The physical parameters and boundary conditions used for all simulations are shown in Tables 3 a and b. The humidity conditions considered are the same as those used by Lum *et al.* (2004).

Table 4

The relevant numerical parameters for this study are shown in Table 4.

Results are presented for the developed PEM fuel cell model. Validation is first undertaken by considering constant diffusivity coefficients, in this case the model is numerically similar to current single phase models, such as Lum *et al.* (2004) and Dutta *et al.* (2000) and so easily validated. Results from parametric studies into the effect of diffusivity coefficients and permeability are then presented to justify the development in integration of an effective diffusivity mode. Finally the two effective diffusivity models are incorporated and compared to experimental data.

3.2 Model validation

Figure 3 shows the width averaged current density at the cathode catalyst layer along the channel length for the constant diffusivity very high humidity case. Close agreement is found with the results of Shimpalee *et al.* (2000) who validated their model both globally and locally against experimental data at low and medium current density values; before the transport limitations caused by flooding become significant.

Figure 3

Good agreement is also found for the other humidity conditions (as can be seen in the global validation in Figure 12). The slight discrepancies between the two models are likely to be due the use of Fick's law rather than the Stefan Maxwell equations, however the close agreement shows that Fick's law is still a reasonable approximation.

3.3 Velocity vectors and pressure distribution

The calculated flow patterns, shown below in Figure 4, show a strong longitudinal flow in the gas channels, and a much slower and proportionally more lateral flow in the porous zones. As the mixture velocity magnitude is significantly larger in the gas channels than in the porous zones, the much slower flow in the porous zones is shown separately (Figure 5) for clarity.

Figure 4

Comparing the velocity vectors at the first two longitudinally spaced slices shows that despite the inlet being modelled as uniform velocity, the flow takes on its parabolic profile (due to the wall no slip conditions) becoming fully developed on both the anode and cathode side, and the lateral velocities quickly reduce. These developed velocity profiles on both the anode and cathode are shown enlarged. It is important to note that the gas channel-gas diffusion layer interface does not force a no-slip condition as this interface is porous but instead significantly reduces the rate of transport. The flow is significantly faster on the cathode side to match the stoichiometric balance of the reactants required for the reaction on the catalyst layers.

The primary flow is pressure driven, with velocity boundary conditions applied at the inlets and lower pressure boundary conditions applied at the outlets, and as such the pressure of the mixture drops nearly linearly from inlet to outlet where the gauge pressure reduces to zero along the anode and cathode gas channels.

Figure 5

In the porous zones (Figure 5) the velocity magnitude is much slower and is close to lateral in direction, showing a net convection of reactants to the catalyst layer. The flow (especially on the anode side) is defined mostly by the reaction rather than by the large inlet velocities. Transport limitations are of critical importance as they reduce the transport across the porous zones, limit the reaction rates and thus the define current density and power output.

Figure 6a,b

The pressure distribution within the PEM fuel cell is shown in Figure 6. The lateral slice shows that the pressure decreases linearly by approximately 970 Pa on the cathode side and 140 Pa on the anode side. The porous zones cause local variations in pressure, with pressure increasing or decreasing across the porous zones depending on the relative mixture velocity. These variations are too small (in the order of 1 Pa) in comparison to the longitudinal pressure drop and the pressure difference between the anode and cathode to be visible globally. A blown up lateral slice (at $z=0.05\text{m}$) is shown in order to better visualise this small pressure drop. The contours are curved, different from the usual linear drop expected in simple filtration systems due to the mixture velocity direction being inwards towards the catalyst layers.

3.3.1 Effect of GDL permeability

Figure 7a,b,c

Figure 8a,b,c

Figure 7 a, b and c show velocity vectors for three different GDL permeability values ($5 \times 10^{-10} \text{m}^2$, $5 \times 10^{-11} \text{m}^2$, $5 \times 10^{-12} \text{m}^2$). The figures 8a, b and c represent pressure variations at the cathode and anode GDLs at different longitudinal slices at the inlet, the centre, and the outlet. The arrow direction gives the flow direction and the arrow colour gives velocity magnitude.

The flow directions are dependent on the GDL permeability. For high permeability GDL material there is a much larger longitudinal convection of mixture, with the high speed gas channel flow and large pressure drop strongly affecting the GDL flowfield. This results in a more complicated flow pattern as can be seen by anode pressure profile at the outlet. The peak at on the cathode outlet at $x = 0.00187\text{m}$ for the high permeability case (Figure 8a) reflects the fact that the direction of flow changes, as can be seen in Figure 7a. This change in flow direction is due to the combination of the flow out of the GDL back into the gas channel and out of the outlets (because the flow is convecting downstream), and the flow diffusing to the catalyst layers where it is destroyed, these transport mechanisms effectively act in opposite directions at the wall and, as they are comparable in magnitude for the high permeability case, they produce the curved peaked profile.

Arrow length is kept constant as the velocity magnitudes vary significantly between zones

For the lower permeability cases the pressure profiles at the inlet and outlet become more linear. This is because the flow becomes diffusion dominated so longitudinal convection significantly reduces, shown by the direction of the velocity vectors at the anode and cathode being close to perpendicular to the gas channels.

3.4 Species concentrations

Flooding occurs on the cathode catalyst layers, so this is where transport limitations are more relevant, for this reason the species distributions at the cathode are studied.

Figure 9

Figure 9 shows the distribution of water in both liquid and vapour as assumed in the variable diffusivity models. Contours of water vapour volume fraction are shown at slices along the longitudinal direction. The water vapour volume fraction increases downstream due to pressure gradient driving the longitudinal convection, and due to the depletion of oxygen from the mixture. The water vapour also diffuses inwards towards the gas channels; this effect is caused by the shoulders and results in the curved lateral contours.

The iso-surface shows the dew point front, the position where the relative humidity exceeds 100%. Both variable diffusivity models assume that the water vapour condenses to form droplets of liquid water in any cell with a relative humidity above this value, so liquid water is modelled as present above the relative humidity iso-surface. This plot shows that the liquid water is mostly contained in cathode gas diffusion layer. Physically in this area the water vapour condenses to form droplets of liquid water which block pores in the gas diffusion layer impeding the transport of reactants and hence curtailing the cell performance. So the water vapour volume fraction in these regions simply represents the liquid water saturation. A more detailed phase change and liquid water transport model would clearly improve the model in this region, this however is more suited to a multiphase model and hence beyond the scope of this paper.

Figure 10

Figure 10 shows the distribution of oxygen in the cathode. Oxygen diffuses from the cathode gas channel through the gas diffusion layer to the catalyst layer where it is destroyed and liquid water created. The oxygen diffuses outwards into the gas diffusion layer and into the shoulders; shown by the curved contours. The oxygen concentration decreases downstream as oxygen is removed from the gas channel and due to the increased volume fraction of water vapour.

3.5 Parametric studies

In order to model liquid water flooding, the liquid water saturation is related to a limitation in transport. The reactants travel through the cell via convection and diffusion; these modes of transport are limited by diffusivity and permeability. The transport of gases in the porous zones is clearly diffusion dominated and so it was decided to

employ a diffusivity model. To check this assumption a study was undertaken to determine the relative importance of phase permeability and reactant diffusivity. The parameters used in these parametric studies are given below in Table 5.

Table 5

Figure 11

A wide logarithmic range of gas diffusion layer permeability values were applied to the model and the resulting width averaged current density plots are shown in Figure 11. From Figure 11 it is clear that any permeability value below $5 \times 10^{-11} \text{ m}^2$ (a typical gas diffusion layer permeability and the value chosen for this study) any changes in the current density cease. As the effects of saturation are only going to reduce the reactant phase permeabilities further than the absolute permeability, this parametric study shows that the incorporation of a relative permeability model into the single phase model will not have any effect.

Figure 12

The simulation was undertaken with a variety of different diffusivity coefficients (see Figure 12). Diffusivity coefficients were scaled up and down (the resulting current density plotted as shown in Figure 14). In this case ‘100% diffusivity’ refers to the diffusivity calculated by equation 24. Each diffusivity coefficient was then increased by 20% and 40% then decreased by 20%, 40% and 60%.

With decreasing diffusivity, the local current density and total averaged current density both decrease. The reduction in diffusivity is felt strongly at the inlet of the PEM fuel cell, where the current density is large and the reaction rate and so rate of diffusion from the gas channel to the catalyst layers is very high.

Unlike for the permeability parametric study there is a marked decrease in cell performance for realistic changes in diffusivity, so it was decided that the initial assumptions were correct and that a diffusion model alone is sufficient to model flooding in a single phase model.

3.6 Local and global validation of flooding PEMFC model

Figure 13

As shown in Figure 13 both diffusivity models show a decrease in all local width averaged current density values due to the improved model for diffusion within the porous and saturated zones. The second diffusivity model showed a more marked reduction further downstream.

The implementation of second model resulted in a larger decrease in current density, and so produced results closer to the experimental data of Shimpalee *et al.* (1999,2000). Also, as the first widely used model makes the assumption of a face centred cubic bonding structure for the Bruggeman correlation and uses simple approximations for the saturation dependence, whereas the second diffusivity model has been derived by applying percolation theory concepts specifically to the gas diffusion layer material under consideration, and so provides a model more specific to the GDL material.

Figure 14

The result shown in Figure 14 show that that the use of the analytical diffusivity model results in similar predictions to experiment and to the work of Lum *et al.* (2004) at low and high humidity conditions (humidity conditions referred to are in table 3a.).

At very high humidity conditions, the single phase PEM fuel cell model with the second analytical diffusivity model (Model 2) presented in this paper results in a performance drop when water flooding occurs at the cathode catalyst layer. This is an effect not seen in current single phase models, and is more representative of the results found by experiment at high power densities and high humidity conditions.

4. Conclusions

This paper presents the results from a three-dimensional, single-phase, fuel cell model, coupled with an effective diffusivity algorithm derived from the percolation theory for simulating water flooding within PEM fuel cells. The objective of this study was to improve upon the existing single-phase models by making allowances for the drop off in performance associated with liquid water flooding. Conventional single phase models cannot predict this phenomenon, and are thus restricted to low current density and low humidity conditions. The numerical model and its implementation were validated by comparison to the work of Shimpalee *et al.* (1999) using an identical computational grid.

Parametric studies were undertaken, consisted of investigations into the effects of diffusivity and permeability, to determine the best way to model the transport restrictions caused by liquid water flooding. Lowering diffusivity coefficients resulted in a reduction in the cell current densities. Lowering the GDL

permeability only affected the local current density up to limiting permeability value; a value greater than the realistic, unsaturated gas diffusion layer permeability value used. A phase permeability model could only reduce the permeability further than this initial value, so the incorporation of a phase permeability model would not affect the cell current density or any other performance parameters. Hence it was concluded that an accurate diffusivity model would increase the accuracy of the results, whereas for a single phase model at least, a phase permeability model would leave the cell performance unaffected. This however is not shown and a phase permeability model specific to the gas diffusion layer material has been developed for use in multiphase simulation.

Simulations were carried out for three sets of physical parameters representing three different humidity cases to study the accuracy of the model for a wide range of conditions, as has also been done by Lum *et al.* (2004) and Dutta *et al.* (2000). The incorporation of the effective diffusivity model resulted in the prediction of cell current densities which were closer to those predicted experimentally at higher current densities without the loss of accuracy at lower current densities.

There is still however much room for improvement, as the developed model does not consider the transport of liquid water, which for greater accuracy should certainly be modelled separately. Although the diffusivity model improves the predictive power of the numerical model, a multiphase model would represent a significant improvement and allow for the correct treatment of diffusion and convection of the reactant gases and liquid water. This liquid water will not be diffusion dominated within the gas diffusion layer. Hence a significant benefit could be achieved by employing the developed effective diffusivity models (Model 2) resulting from this work, in conjunction with a model capable of simulating phase-permeabilities in a multiphase solution.

505 Nomenclature

506	a_k	- Water activity	542	ϵ	- Porosity
507	a	- Pressure diffusivity constant	543	ξ	- Correlation length
508	b	- Pressure diffusivity constant	544	λ	- Electrical conductivity
509	c	- Concentration	545	μ	- Dynamic viscosity
510	D_k	- Diffusivity coefficient	546	ρ	- Density
511	$D_{k,j}$	- Binary diffusion coefficient	547	$\sigma_m(x,y)$	- Membrane conductivity
512	D_k^{eff}	- Effective diffusivity of species	548	ν	- Critical exponent
513	DSF	- Diffusivity scaling factor	549	Subscripts	
514	F	- Faraday's constant	550	A	- First component
515	$f()$	- Diffusivity scaling function	551	a	- anode
516	$g()$	- Diffusivity scaling function	552	B	- Second component
517	$I(x,y)$	- Current density	553	c	- Cathode
518	I_0	- Exchange current density	554	Dry	- Dry membrane
519	J	- Binary diffusion coefficient	555	H_2	- Hydrogen
520	k	- Permeability	556	i	- Direction
521	M	- Molar mass of species	557	k	- Species
522	$M_{m,dry}$	- Mass of dry membrane	558	m	- Membrane
523	n	- Number of bonds	559	O_2	- Oxygen
524	$n_d(x,y)$	- Electro-osmotic drag coefficient	560	w	- Water
525	P	- Pressure	561	x	- x direction
526	P_b	- Bond occupation probability	562	y	- y direction
527	P_w^{sat}	- Saturation pressure of water	563	z	- z direction
528	R	- Universal gas constant	564	0	- Unsaturated
529	S	- Saturation	565	1	- Partially saturated
530	S_u	- Momentum source	566	Superscripts	
531	S_k	- Species transport source	567	sat	- Saturation
532	T	- Temperature	568	eff	- Effective
533	t_m	- Membrane thickness			
534	u	- Velocity			
535	V_{oc}	- Open circuit voltage			
536	V_{cell}	- Cell voltage			
537	Vol	- Volume fraction			
538	X	- Molar mass fraction			
539	Y	- Mole fraction			
540	$\alpha(x,y)$	- Net water transport coefficient			
541	$\eta(x,y)$	- Local overpotential			

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Figure Captions

Figure 1. Numerical algorithm.

Figure 2. Geometry and computational domain.

Figure 3. Width averaged current density at very high humidity conditions GDL permeability = $5 \times 10^{-11} \text{ m}^2$ – Validation against Shimpalee *et al.* (2000).

Figure 4: Velocity vectors shown at streamwise slices at very high humidity in the gas channels, GDL permeability = $5 \times 10^{-11} \text{ m}^2$, fully developed velocity profiles are shown enlarged.

Figure 5: Velocity vectors shown at streamwise slices at very high humidity in the porous zones GDL permeability = $5 \times 10^{-11} \text{ m}^2$.

Figure 6a. 3D Gauge pressure contours for very high humidity, GDL permeability = $5 \times 10^{-11} \text{ m}^2$ case.

Figure 6b. Gauge pressure contours for very high humidity, GDL permeability = $5 \times 10^{-11} \text{ m}^2$ case at $Z = 0.05$ slice.

Figures 7a,b,c. Velocity vectors at midway slice for high humidity GDL permeability = $5 \times 10^{-10} \text{ m}^2$ (a), $5 \times 10^{-11} \text{ m}^2$ (b) and $5 \times 10^{-12} \text{ m}^2$ (c) case, arrow direction and colour show direction and magnitude.

Figures 8. Width averaged pressure drops at across the anode and cathode GDLs at the inlet, midway along the channel and the outlet for high humidity GDL permeability = $5 \times 10^{-10} \text{ m}^2$ (a), $5 \times 10^{-11} \text{ m}^2$ (b) and $5 \times 10^{-12} \text{ m}^2$ (c) case.

Figure 9: Oxygen volume fraction contour plot shown at longitudinal slices for high humidity GDL permeability = $5 \times 10^{-11} \text{ m}^2$ case.

Figure 10: Water vapour volume fraction contour plot with relative humidity = 100% iso-surface for high humidity GDL permeability = $5 \times 10^{-11} \text{ m}^2$ case.

Figure 11: Effect of GDL permeability on width averaged current density shown for very high humidity GDL permeability = $5 \times 10^{-11} \text{ m}^2$ case.

Figure 12: Effect of gas diffusivity coefficients on width averaged current density shown for very high humidity GDL permeability = $5 \times 10^{-11} \text{ m}^2$ case.

Figure 13: Comparison of diffusivity models, width averaged current density shown at very high humidity, GDL permeability = $5 \times 10^{-11} \text{ m}^2$.

Figure 14: Global validation with variable inlet humidity, comparison against the numerical model and experiment data from Lum *et al.* (2005).

Table Captions

Table 1: Governing Equations

Table 2: Auxiliary Equations

Table 3 a&b: Physical Parameters

Table 4: Numerical Parameters

Table 5: Parametric study parameters **TABLE 1**

Description	Equation	
Momentum equation	$\nabla \cdot (\rho \vec{u} \vec{u}) = -\nabla P + \nabla \cdot (\mu \nabla \vec{u}) + S_u$	(1)
Darcy momentum term	$\nabla P = -\frac{\mu \vec{u}}{k_i}$	(2)
Continuity equation	$\nabla \cdot (\rho \vec{u}) = S_m$	(3)
Source term at anode CL	$S_m = S_{O_2} + S_{cw}$	(4)
Source term at cathode CL	$S_m = S_{H_2} + S_{aw}$	(5)
Species transport equations	$\nabla \cdot (\rho \vec{u} \vec{X}_k) = \nabla \cdot (D_k^{eff} \rho \nabla \vec{X}_k) + S_k$	(6)
Consumption of hydrogen due to electrochemical effects at the anode	$S_{H_2} = -\frac{I(x, y)}{2F} M_{H_2} A_{cv}$	(7)
Consumption of oxygen due to electrochemical effects at the cathode	$S_{O_2} = -\frac{I(x, y)}{4F} M_{O_2} A_{cv}$	(8)
Production of water and flux of water due to electrochemical effects at the cathode	$S_{cww} = \frac{1 + 2\alpha(x, y)}{2F} I(x, y) M_{H_2O} A_{cv}$	(9)
Flux of water due to electrochemical effects at the anode	$S_{awv} = -\frac{\alpha(x, y)}{F} I(x, y) M_{H_2O} A_{cv}$	(10)

TABLE 2

Description	Equation	
Binary diffusion coefficients	$P \cdot D_{AB} = a \left(\frac{T}{\sqrt{T_{cA} T_{cB}}} \right)^b (P_{cA} P_{cB})^{1/3} (T_{cA} T_{cB})^{5/12} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{1/2} \varepsilon^{1.5}$	(11)
Net water transport coefficient	$\alpha(x, y) = n_d(x, y) - \frac{FD_w(x, y) \{c_{w,c}(x, y) - c_{w,a}(x, y)\}}{I(x, y)t_m}$	(12)
Local current density	$I(x, y) = \frac{\sigma_m(x, y)}{t_m} [V_{oc} - V_{cell} - \eta(x, y)]$	(13)
Reaction overpotential	$\eta(x, y) = \frac{RT}{0.5F} \ln \left[\frac{1.013 \times 10^5 \times I(x, y)}{I_{0C} P_{O_2}(x, y)} \right] + \frac{RT}{F} \ln \left[\frac{1.013 \times 10^5 \times I(x, y)}{I_{0A} P_{H_2}(x, y)} \right]$	(14)
Membrane conductivity	$\sigma_m(x, y) = 100 \left[0.00514 \left(\frac{M_{m,dry}}{\rho_{m,dry}} \right) c_{w,a}(x, y) - 0.00326 \right] \times \exp \left[1268 \left(\frac{1}{303} - \frac{1}{T} \right) \right]$	(15)
Water concentration	$c_{w,k}(x, y) = \frac{\rho_{m,dry}}{M_{m,dry}} (0.043 + 17.8a_k - 39.8a_k^2 + 36.0a_k^3)$ if $a_k \leq 1$	(16)
	$c_{w,k}(x, y) = \frac{\rho_{m,dry}}{M_{m,dry}} (14 + 1.4(a_k - 1))$ if $a_k > 1$	(17)
Water activity	$a_k(x, y) = \frac{X_{w,k}(x, y)P(x, y)}{P_{w,k}^{sat}}$	(18)
Water vapour saturation pressure	$P_{w,k}^{sat} = [0.00644367 + 0.000213948(T - 273.0) + 3.43293 \times 10^{-5}(T - 273.0)^2 - 2.70381 \times 10^{-7}(T - 273.0)^3 + 8.77696 \times 10^{-9}(T - 273.0)^4 - 3.14035 \times 10^{-13}(T - 273.0)^5 + 3.82148 \times 10^{-14}(T - 273.0)^6] \times 1.013 \times 10^5$	(19)
Electro-osmotic drag coefficient	$n_d(x, y) = 0.0049 + 2.02a_a - 4.53a_a^2 + 4.09a_a^3$ if $a_a \leq 1$ $n_d(x, y) = 1.59 + 0.159(a_a - 1)$ if $a_a > 1$	(20)
Water diffusion coefficient	$D_w = n_d \times 5.5 \times 10^{-11} \exp \left[2416 \left(\frac{1}{303} - \frac{1}{T} \right) \right]$	(21)

TABLE 3 A,B

Description	Low Humidity	High Humidity	Very High Humidity	Units
Anode inlet velocity	1.83	2.21	2.56	ms ⁻¹
Anode inlet mass fraction of hydrogen	0.635	0.406	2.595	-
Anode inlet mass fraction of water vapour	0.365	0.594	0.705	-
Cathode inlet velocity	7.91	9.05	12.9	ms ⁻¹
Cathode inlet mass fraction of oxygen	0.225	0.21	0.187	-
Cathode inlet mass fraction of nitrogen	0.734	0.705	0.61	-
Cathode inlet mass fraction of water vapour	0.041	0.085	0.203	-

Symbol	Description	Value	
P_0	Operating pressure	101325 Pa	
T_0	Operating temperature	345 K	
k_i	GDL Permeability	$5 \times 10^{-11} \text{ m}^2$	
F	Faradays constant	96485.3 C mol ⁻¹	
-	-	Water	Other species
a	Binary diffusivity equation coefficients	3.64×10^{-4}	2.745×10^{-4}
b		2.334	1.832
ε	GDL porosity	0.65	
t_m	Membrane thickness	0.1270 mm	
V_{oc}	Open circuit voltage	1.1 V	
V_{cell}	Cell voltage	0.53 V	
I_{0A}	Exchange current densities	100 A m ⁻²	
I_{0C}		1000 A m ⁻²	
R	Gas constant	8.3144 mol ⁻¹ K ⁻¹	
$M_{m,dry}$	Dry mass of membrane	1.1 kg mol ⁻¹	
$\rho_{m,dry}$	Dry density of membrane	2000 kg m ⁻³	
v	Correlation index	0.90	
P_c	Percolation threshold	0.11	

TABLE 4

Description	Value
Number of cells	14114
Number of iterations	~250
Convergence criteria	10^{-6}
Numerical scheme	Second order upwinding
Computational time	~ 30 mins
Anode inlet mass flux	$-3.9 \times 10^{-13} \text{ kg/m}^3\text{s}$
Anode outlet mass flux	$-9.4 \times 10^{-12} \text{ kg/m}^3\text{s}$
Cathode inlet mass flux	$3.16 \times 10^{-13} \text{ kg/m}^3\text{s}$
Cathode outlet mass flux	$9.53 \times 10^{-12} \text{ kg/m}^3\text{s}$
Total	$-2.27 \times 10^{-19} \text{ kg/m}^3\text{s}$

TABLE 5

Parameter	Value
DSF1	140%
DSF2	120%
DSF3	100%
DSF4	80%
DSF5	60%
DSF6	40%
k1	$1.5 \times 10^{-8} \text{ m}^2$
k2	$1.5 \times 10^{-9} \text{ m}^2$
k3	$1.5 \times 10^{-10} \text{ m}^2$
k4	$1.5 \times 10^{-11} \text{ m}^2$
k5	$1.5 \times 10^{-12} \text{ m}^2$

FIG:1

FIG:2

FIG:3

FIG:4

FIG:5

FIG:6

FIG:7(a)

FIG:7(b)

FIG:7©

FIG:8(A, B, C)

a

b

c

FIG:9

FIG:10

FIG 11

FIGURE 12

FIGURE 13

FIGURE 14