TWO-DIMENSIONAL MODEL FOR THE ENTIRE SANDWICH OF A PEM FUEL CELL

Vladimir Gurau1* Frano Barbir† Hongtan Liu‡

1 Energy Partners, 1501 Northpoint Parkway, Suite 102, Technology Center, West Palm Beach, Florida 33407
* University of Miami, Mechanical Engineering Department, Coral Gables, Florida 33124

ABSTRACT

A two dimensional, non-isothermal mathematical model for the entire sandwich of a proton exchange membrane (PEM) fuel cell including the gas channels has been developed. In order to take into consideration the real concentration distributions along the interface between the gas diffuser and catalyst layer, transport equations are solved simultaneously for the domain consisting of the coupled gas channel, gas diffuser, catalyst layer and membrane. The selfconsistent schematical model for porous media is used for the equations describing transport phenomena in the membrane, catalyst layers and gas diffusers, while standard Navier-Stokes, energy transport, continuity and species concentration equations are solved in the gas channels. A special handling of the transport equations enabled us to use the same numerical method to solve them, and therefore to treat the gas channel-gas diffuser-catalyst layer domains as an entirety, avoiding arbitrary boundary conditions at their interfaces. The oxygen mole fraction distribution in the coupled cathode gas channel-gas diffuser is studied for different values of the operating current density. Influences of the inlet conditions at the gas channel entries and of the gas diffuser porosity on the cell performance are also analyzed.

INTRODUCTION

One of the most challenging problems in fuel cells modeling seems to have been the possibility to simulate, rather than prescribe or guess the concentration variations along the interface between the gas diffusers and catalyst layers. This is a major problem, since the distribution of the reactant concentrations along the electrodes is needed to calculate the transfer currents in electrochemical cells. In the particular case of a PEM fuel cell, this phenomenon is related to the gas transport in the coupled domain of a gas channel-gas...(remaining text continues)
diffuser-catalyst layer, and the ability to solve the transport equations in this heterogeneous domain apparently has been the main draw-back in simulating reactant distributions. A mathematical model together with a numerical procedure featuring this ability, would represent a significant step in simulating transport phenomena and performance of PEM fuel cells.

In their study, Ridge and White (1), Verbrugge and Hill (2), (3), Bernardi and Verbrugge (4), (5), Springer et al. (6) treated 1-D models of the same problem which provided useful information for further development of the 2-D models.

The 2-D models published so far, are mostly concerned with the transport phenomena in the domains consisting of the membrane, catalyst layers and gas diffusers, while the concentrations/partial pressures in the gas channels are assumed more or less arbitrarily, or averaged values are used as boundary conditions at the interface with the gas diffusers. The work of Singh et al. (7) assumed linear variations of the chemical species at the gas channel-gas diffuser interfaces, and the developed model describes phenomena exclusively in the membrane-catalyst layers-gas diffusers. Fuller and Newman (8) solved for the transport across the fuel cell sandwich at certain locations along the gas channel and thereafter integrated in the second direction, while the gas outside the gas diffusers was assumed to be of uniform composition in the direction across the cell. Nguyen and White (9) used algebraic expressions for the concentrations along the electrodes, while Amphlett et al. (10), in their modeling of the Ballard IV fuel cell, assumed averaged partial pressures along the gas channels.

In real life, the concentrations along the gas channels-gas diffusers-catalyst layers will vary due to diffusion-convection transport and electrokinetics in the catalyst layers. These distributions will depend therefore on the gas/medium properties, as well as on the reaction rates. These latter ones are in turn functions of the reactant concentrations and an iterative procedure would be required to predict them. A proper description of the species concentration distribution would involve the use of the 2-D momentum equations in the coupled gas channel-gas diffuser-catalyst layer domain. Together with the continuity and species concentration equations (Stefan-Maxwell), equations describing the electrochemical reactions have to be also part of the system. These latter ones are coupled with the transport equations in membrane via electro-osmotic terms. The only independent variables for constant geometry and material properties are the mass flow rates, temperatures, humidities and the pressures of the gas mixtures at the gas channel inlets, the external circuit resistance and the temperature of the heating (cooling) agent, the last one having influence on the electrochemical reactions via Arrhenius type terms. These are actually the only parameters that can be controlled in laboratory experiments or other fuel cell applications.
MODEL DESCRIPTION AND ASSUMPTIONS

The model used here is two dimensional, and is presented in Fig. 1. It represents a cross-section along one of the cathode channels and contains all fuel cell elements, from one collector plate to the other. It is assumed here that the design of the collector plates is such, that the anode and cathode gas channels have the same orientation and appear in the same cross-section.

The following assumptions are used in our mathematical formulation:

- The gas mixtures are considered to be perfect gases.
- The volume occupied by liquid water in the gas channels, coming from the gas diffusers is negligible (in gas channels, only gas mixtures are present).
- The flow is laminar everywhere.
- The gas mixture flows are incompressible.
- Only the steady state case is taken into account.
- The gas diffusers, catalyst layers and the PEM are considered each as isotropic porous media.
- Dilation or contraction of the porous media is neglected.
- The contact electrical losses at the interfaces between different fuel cell elements are neglected.
- The catalyst layers are considered to have vanishingly small thicknesses when the transport equations are solved, but the real values are taken into account when the membrane phase potential and current density are calculated.
- The dispersion of the fluids in the porous media is disregarded at this stage. Anyhow, it can be taken into account if the general diffusion coefficients are properly corrected.
- The heat generated under reversible conditions is neglected in this work.

Our mathematical model uses nondimensional transport equations. Three different domains are considered, corresponding to the phase of the fluid taken into account (Fig 2): the cathode gas channel-gas diffuser-catalyst layer for the air mixture; the cathode gas diffuser-catalyst layer-membrane-anode catalyst layer-gas diffuser for liquid water; the anode gas channel-gas diffuser-catalyst layer for hydrogen.

In order to take into consideration the real concentration distributions along the interface between the gas diffuser and catalyst layer, transport equations are solved simultaneously for the domain consisting of the coupled gas channel, gas diffuser, catalyst layer and membrane. The selfconsistent schematical model for porous media is used for the equations describing transport phenomena in the membrane, catalyst layers and gas diffusers, while standard Navier-Stokes, energy transport, continuity and species concentration equations are solved in the gas channels. A special handling of the transport
equations enabled us to use the same numerical method to solve them, and therefore to treat the gas channel-gas diffuser-catalyst layer domains as an entirety, avoiding arbitrary boundary conditions at their interfaces.

The fuel cell parameters and the fluid properties for the base case condition are presented in Tables 1 and 2.

Table 1
The Physical Parameters of the Fuel Cell Elements

gas channel length, \(7.62 \times 10^{-2} \text{ m}\)
gas channel width, \(D = 7.62 \times 10^{-4} \text{ m}\)
gas diffuser width, \(2.54 \times 10^{-4} \text{ m}\)
catalyst layer width, \(D_{cl} = 0.287 \times 10^{-4} \text{ m}\)
membrane width, \(L = 2.3 \times 10^{-4} \text{ m}\) (1)
gas diffuser porosity, \(\varepsilon = 0.4\)
membrane porosity, \(\varepsilon_{mm} = 0.28\) (1)
volume fraction membrane in catalyst layer, \(\varepsilon_{mc} = 0.5\) (1)
thermal conductivity of the graphite matrix of the gas diffuser, \(k_g = 150.6 \text{ W.m}^{-1}\text{K}^{-1}\)
hydraulic permeability of the membrane, \(k_p = 1.58 \times 10^{-18} \text{ m}^2\) (1)
electrokinetic permeability of the membrane, \(k_e = 1.13 \times 10^{-19} \text{ m}^2\) (1)
thermal conductivity of the dry membrane, \(k_{m, dry} = 100 \text{ W.m}^{-1}\text{K}^{-1}\)
fixed charged site concentration in membrane, \(c_f = 1.2 \times 10^3 \text{ mol.m}^{-3}\) (1)
charge of sulfonate site in membrane, \(z_f = -1\)
reference exchange current density times area, \(a j_0 = 5 \times 10^3 \text{ A.m}^{-3}\) (1)
cathodic transfer coefficient for cathode, \(\alpha_c = 2\) (1)

Table 2
The Physical Parameters of the Fluids (Base Case Condition)

air inlet temperature, \(T_i = 353 \text{ K}\)
air inlet pressure, \(p_i = 3 \text{ atm}\)
air inlet velocity, \(U_i = 0.35 \text{ m.s}^{-1}\)
air viscosity, \(\mu = 1.85 \times 10^{-5} \text{ kg.m}^{-1}\text{s}^{-1}\)
air thermal conductivity, \(k = 2.5 \times 10^{-2} \text{ W.m}^{-1}\text{K}^{-1}\)
molecular mass of air, \(29 \times 10^{-3} \text{ kg.mol}^{-1}\)
molecular mass of oxygen, \(32 \times 10^{-3} \text{ kg.mol}^{-1}\)
molecular mass of nitrogen, $28 \times 10^3 \text{ kg.mol}^{-1}$
molecular mass of water, $18 \times 10^3 \text{ kg.mol}^{-1}$
air specific heat at constant pressure, $c_p = 1008 \text{ J.kg}^{-1}.\text{K}^{-1}$
air relative humidity at inlet, 100%
oxygen/nitrogen ratio in air at inlet, 0.21/0.79
hydrogen inlet pressure, $p_i = 1 \text{ atm}$
water density, $\rho = 971.1 \text{ kg.m}^{-3}$
water viscosity, $\mu = 8.91 \times 10^{-4} \text{ kg.m}^{-1}.\text{s}^{-1}$
water thermal conductivity, $k = 0.6 \text{ W.m}^{-1}.\text{K}^{-1}$
water specific heat at constant pressure, $c_p = 4190 \text{ J.kg}^{-1}.\text{K}^{-1}$
proton diffusivity in water, $D_{\text{H}^+} = 4.5 \times 10^{-9} \text{ atm.m}^{-2}.\text{s}^{-1}$ (1)
critical temperature for oxygen, $T_{\text{cr}} = 154.4 \text{ K}$
critical pressure for oxygen, $p_{\text{cr}} = 49.7 \text{ atm}$
critical temperature for nitrogen, $T_{\text{cr}} = 126.2 \text{ K}$
critical pressure for nitrogen, $p_{\text{cr}} = 33.5 \text{ atm}$
critical temperature for water, $T_{\text{cr}} = 647.3 \text{ K}$
critical pressure for oxygen, $p_{\text{cr}} = 221.2 \text{ atm}$

RESULTS AND DISCUSSION

The mathematical model and the solution technique have been validated by comparing the characteristics of the fuel cell determined numerically with the experimental results of Ticianelli et al. (11) and have been discussed by Gurau (12). The behavior of the mathematical model in predicting the values of the velocity and the scalar variables at the interface between a gas channel and the adjacent porous gas diffuser has been presented in the same work.

Cell Performance

Effect of the Gas Diffuser Porosity on the Cell Performance. Figure 3 shows the cell voltage versus the operating current density for different values of the gas diffuser porosity $\varepsilon$, assuming the isothermal case with the temperature $T = 353 \text{ K}$, an inlet air velocities $U_i = 0.35 \text{ m/s}$ and the water vapor mole fraction at the gas channel inlet, $X_{w,i} = 0.1579$ (100 % humidity).

For lower values of $\varepsilon$, lower values of the limiting current density are found. This phenomenon is due to the limited possibilities of the reactant in the cathode side gas mixture (oxygen) to be transported towards the catalyst layer. Bernardi and Verbrugge (5)
present limiting current density as a function of porosity for three different catalyst layer thicknesses, obtained for their 1-D model. Extrapolating these curves for the catalyst layer thickness used in our model, one may find close values for the limiting current. The slope of the curve is in good agreement with their results as well. Unlike other numerical methods, where the program fails to give results when the limiting current is achieved, the present one is able to predict phenomena even in the region where the concentration overpotentials are predominant.

**Effect of the Inlet Air Velocity on the Cell Performance.** Figure 4 presents the current density for different values of the air velocity at the cathode gas channel entrance, considering the gas diffuser porosity $\varepsilon = 0.4$, a constant temperature $T = 353 \text{ K}$ (isothermal case) and the water vapor mole fraction at the cathode gas channel inlet, $X_{\text{w, i}} = 0.1579$ (100% humidity). For higher inlet air velocities (higher air mass flow rates), more oxygen is fed and therefore more oxygen is likely to arrive at the catalyst layer, with the result of a higher limiting current density. This is explained by the fact that for the same pressure field, for higher velocities, the axial momentum transfer across the gas channel-gas diffuser interface becomes more important, with a consequence of more "fresh" air arriving to the catalyst layer. For inlet air velocities higher than approx. 2 m/s, the limiting current becomes constant, which shows that there is a limit effect of the momentum transfer across the gas channel-gas diffuser interface.

**Effect of Temperature on the Cell Performance.** Figure 5 presents the effect of the cell temperature on the voltage-current density characteristic for an inlet air velocity $U_i = 0.35 \text{ m/s}$, gas diffuser porosity $\varepsilon = 0.4$, and 100% air humidity. Content of water vapor in air at the cathode channel inlet is taken as a function of temperature from available data. Water vapor concentration at the cathode gas diffuser-catalyst layer interface will determine the liquid water content in the membrane and therefore the membrane ionic conductivity, with the final effect of better cell performances (higher current densities) at higher temperatures. At higher temperatures, the open circuit potential is higher as well.

**The Oxygen Mole Fraction Field in the Cathode Gas Channel-Gas Diffuser Coupled Domain.** Figure 6 shows the oxygen mole fraction field in the coupled cathode gas channel-gas diffuser domain for the base case conditions (isothermal case) and the limiting current density. The oxygen is consumed in the catalyst layer. Although the rate of oxygen depletion is higher at the left side of the catalyst layer-gas diffuser interface, the oxygen concentration is lower in the right side. This phenomenon is explained by the convective transport in gas diffuser. The corresponding stoichiometric ratios are calculated as the ratio between the average oxygen mole fraction at the inlet and the average oxygen mole fraction difference between exit and inlet.

**The Oxygen Mole Fraction Distribution as a Function of the Fuel Cell Operating Current Density.** Most of the mathematical models for PEM fuel cells use oxygen mole
fraction or partial pressure distributions along the cathode gas channel-gas diffuser interface as input data. These "guessed" or a priori prescribed distributions may eventually affect the computed values of the operating current density. The present mathematical model enables us to solve the transport equations in the coupled gas channel-gas diffuser domain, therefore the oxygen mole fraction is calculated, not prescribed. Figure 7 presents the computed oxygen mole fraction distributions at the interface between the cathode gas channel and gas diffuser for the base case conditions and different operating current densities. For higher operating current densities, these distributions are clearly non linear, as assumed in other models. For the base case conditions and operating current densities higher than $3.17*10^4 \, A/m^2$, the oxygen mole fraction distribution remains almost unchanged at this interface, which shows that limiting current density is approached.

The Current Density Distribution at the Membrane-Cathode Catalyst Layer as a Function of the Fuel Cell Operating Current Density. If the operating current density was an input data and the distribution of the oxygen mole fraction at the cathode gas channel-gas diffuser was not prescribed before performing the computations, it would be unclear how the current density distribution could be found. Even though the operating current density is the average of the current density distribution at the membrane-cathode catalyst layer interface, the knowledge of the former one is not sufficient to determine the latter one. Therefore, in the present formulation we used the total electrode overpotential as an input data to find the operating current density, the current density distribution and the oxygen mole fraction distribution. This was possible, since there is a bijective relationship between the cell overpotential and the cell voltage. It is true that for a certain regime, the total electrode overpotential is not known a priori. Therefore one has to calculate the operating current density-cell voltage curve for different regimes, from zero current density until the limiting current density is achieved, and after that to interpolate for the desired regime. Figure 8 shows the current density distribution at the membrane-cathode catalyst layer interface, for the base case and the oxygen mole fraction distributions in Fig. 7.

CONCLUDING REMARKS

The mathematical model presented here enabled us to predict the phenomena in the entire fuel cell sandwich, including the gas channels. The input data are only those parameters that can be controlled in the real life fuel cell operation. No assumptions are necessary for the distribution of the species concentrations or current density, as they are assumed in other fuel cell models available in the literature. The computed oxygen mole fraction along the gas channel-gas diffuser interface and the current density along the membrane-catalyst layer interface do not present linear distributions, as are assumed in other works. The oxygen mole fraction field is also presented in the coupled gas channel-
gas diffuser domain. The computed fuel cell performances are realistic. They are compared only to other computed results, obtained using simpler fuel cell models, therefore actual validation of this 2-D model with experimental results remain to be done. The present mathematical model will be used in conjunction with laboratory experiments for optimization of the fuel cell structure and performance.

REFERENCES

1. S. J. Ridge, R. E. White, Y. Tsou, R. N. Beaver, G. A. Eisman, J. Electrochem. Soc., 136, 1902 (1989).
2. M. W. Verbrugge, R. F. Hill, J. Electrochem. Soc., 137, 886 (1990).
3. M. W. Verbrugge, R. F. Hill, J. Electrochem. Soc., 137, 3770 (1990).
4. D. M. Bernardi, M. W. Verbrugge, AIChE J., 37, 1151 (1991).
5. D. M. Bernardi, M. W. Verbrugge, J Electrochem Soc, 139, 2477 (1992).
6. T. E. Springer, T. A. Zawodinski, S. Gottesfeld, J. Electrochem. Soc., 136, 2334 (1991)
7. D. Singh, D. M. Lu, N. Djilali in Proceedings of the First International Energy and Environment Symposium, Karadeniz Technical University, Trabzon, Turkey, 615 (1996)
8. T. F. Fuller, J. Newman, J. Electrochem. Soc., 5, 1218 (1993)
9. T. V. Nguyen, R. E. White, J. Electroch. Soc., 140, 2178 (1993)
10. J. C. Amphlett, R. M. Baumert, R. F. Mann, B. A. Peppley, and P. R. Roberge, J. Electrochem. Soc., 142, 1 (1995)
11. E. A. Ticianelli, C. R. Derouin, S. Srinivasan, J. Electroanal. Chem., 251, 275 (1988)
12. V. Gurau, Ph.D. Thesis, University of Miami, Coral Gables, FL (1998)
Figure 1
Two dimensional representation of a PEM fuel cell

Figure 2
The geometry, the coordinate axes, the boundary types and the characteristic dimensions of the three domains

Electrochemical Society Proceedings Volume 98-27
Figure 3
Effect of the gas diffuser porosity on the voltage-current density characteristic;
$U_i = 0.35 \text{ m/s}$, $T = 353 K$, (isothermal case), $X_{w,i} = 0.1579$ (100% humidity)

Figure 4
Effect of the air inlet velocity on the voltage-current density characteristic;
$T = 353 K$ (isothermal case), $X_w = 0.1579$ (100% humidity), $\varepsilon = 0.40$
Effect of the cell temperature on the voltage-current density characteristic; 
$U_t = 0.35 \text{ m/s}, \varepsilon = 0.40, 100\% \text{ humidity}$

The oxygen mole fraction in the cathode gas channel-gas diffuser domain, for 
$I_{avg} = 3.18 \times 10^4 \text{ A/m}^2$ (limiting current), $U_t = 0.35 \text{ m/s}, T = 353 K$, (isothermal case), 
$X_{w, i} = 0.1579$ (100% humidity), $\varepsilon = 0.40$. Resulting stoichiometric ratio: $\xi = 2.28$
Figure 7
The oxygen mole fraction distribution along the gas channel-gas diffuser interface, for different cell operating current densities; $U_f = 0.35 \text{ m/s}, T = 353 K$ (isothermal case), $X_{O_2, i} = 0.1579$ (100% humidity), $e = 0.40$

Figure 8
The current density distribution along the membrane-catalyst layer interface, for different cell operating current densities; $U_i = 0.35 \text{ m/s}, T = 353 K$ (isothermal case), $X_{O_2, i} = 0.1579$ (100% humidity), $e = 0.40$
APPENDIX

MATHEMATICAL MODEL

In Gas Channels

The fluid mechanics in the gas channel are described by the continuity and Navier-Stokes equations, which in non-dimensional form and under the assumptions mentioned in the previous section become (13):

\[
\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \tag{1}
\]

\[
-\frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = -\frac{\partial p}{\partial x} + \frac{1}{\text{Re}} \left( \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right) \tag{2}
\]

\[
-\frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} = -\frac{\partial p}{\partial y} + \frac{1}{\text{Re}} \left( \frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} \right) \tag{3}
\]

where the non-dimensional parameters are defined as:

\[
\bar{u} = \frac{u}{U_i}, \quad \bar{v} = \frac{v}{U_i}, \quad \bar{x} = \frac{x}{D}, \quad \bar{y} = \frac{y}{D}, \quad \bar{p} = \frac{p - p_s}{\rho_f U_i^2}, \quad \text{Re} = \frac{\rho_i U_i D}{\mu}
\]

Similarly, the energy equation becomes:

\[
\frac{\partial \bar{T}}{\partial \bar{x}} + v \frac{\partial \bar{T}}{\partial \bar{y}} = \frac{1}{\text{RePr}} \left( \frac{\partial^2 \bar{T}}{\partial \bar{x}^2} + \frac{\partial^2 \bar{T}}{\partial \bar{y}^2} \right) \tag{4}
\]
where

\[ \bar{T} = \frac{T - T_w}{T_i - T_w} \quad \text{and} \quad Pr = \frac{\mu c_p}{k} \]

The equation for the species mole fraction is:

\[
\begin{align*}
- \frac{\partial X_k}{\partial x} + v \frac{\partial X_k}{\partial y} &= \frac{1}{Re Sc_k} \left( \frac{\partial^2 X_k}{\partial x^2} + \frac{\partial^2 X_k}{\partial y^2} \right)
\end{align*}
\]  \[5\]

where \(X_k\) stands for the mole fraction of the \(k\)'th component, and the Schmidt number: \(Sc_k = \frac{\mu}{\rho D_k}\). The diffusion coefficients can be expressed in terms of binary diffusion coefficients as:

\[
D_k = \frac{1 - \rho_k}{\sum_{m} \frac{c}{\rho} \frac{1}{D_{k,m}}} \quad \text{[6]}
\]

Equation [5] may be solved only for \(n-1\) components (water vapor and oxygen in the cathode), the last one for nitrogen coming out from the relation:

\[
X_n = 1 - \sum_{i=1}^{n-1} X_i \quad \text{[7]}
\]

In Gas Diffusers

The gas diffusers in our virtual fuel cell are made from carbon cloth of E-Tek fabrication.
Particular forms of the transport equations [1]-[5] may be derived for the gas diffusers if their porous nature is taken into account. This is possible if the macroscopic, instead of the microscopic variables are used, and by ensemble or space averaging the terms in the transport equations.

In terms of macroscopic variables, the continuity equation in the porous gas diffuser reads:

$$\frac{\partial q_x}{\partial x} + \frac{\partial q_y}{\partial y} = 0$$  \[8\]

where $q_x$ and $q_y$ are the components of the specific discharge.

The macroscopic velocity field in the porous medium is provided by expressions obtained by space averaging the Navier-Stokes equations. The resulting equations are a generalized form of Darcy’s law (14), which in non-dimensional form read as:

$$-q_x \frac{\partial q_x}{\partial x} + q_y \frac{\partial q_x}{\partial y} = -\varepsilon \frac{\partial \bar{p}}{\partial x} + \frac{1}{\text{Re}^{(2)}} \left( \frac{\partial^2 q_x}{\partial x^2} + \frac{\partial^2 q_x}{\partial y^2} \right) - \frac{\varepsilon \mu}{k} \frac{q_x}{\rho_j U_i} D$$  \[9\]

$$-q_x \frac{\partial q_y}{\partial x} + q_y \frac{\partial q_y}{\partial y} = -\varepsilon \frac{\partial \bar{p}}{\partial y} + \frac{1}{\text{Re}^{(2)}} \left( \frac{\partial^2 q_y}{\partial x^2} + \frac{\partial^2 q_y}{\partial y^2} \right) - \frac{\varepsilon \mu}{k} \frac{q_y}{\rho_j U_i} D$$  \[10\]

When $r^{(2)} = 1$, equations [9] and [10] turn into Brinkman’s equations. Dagan (15) showed that $r^{(2)} \gg 1$, and the relationship for $r^{(2)}$ can be estimated as:

$$r^{(2)} = 2.25 \frac{(1 - \varepsilon)^2}{\varepsilon^2}$$  \[11\]

At this stage it is clear to see the similarity between equations [2], [3] and [9], [10]. This enables us to consider the whole domain (channel + gas diffuser) as an entire, if in the numerical program the extra body forces are taken into account for the gas diffuser sub-domain. When the flow field is obtained numerically, one has to remember that the values of the velocities in the porous gas diffuser stand for the specific discharge.
In the gas diffuser layers, energy is transported by diffusion and locally by convection in the fluid phase, and by conduction in the solid matrix of the porous graphite cloth. For such a porous medium, the energy equation can be obtained by ensemble averaging the microscopic energy equations in the fluid and solid phase respectively, neglecting the heat generation by viscous dissipation and adding them up. To define the resulting effective, macroscopic heat conductivity, different schematical models of porous media are available in the literature (14). In this work, we have chosen the self-consistent approximation:

\[
k_{\text{eff}} = -2k_{gr} + \frac{1}{\varepsilon} \frac{1 - \varepsilon}{2k_{gr} + k_{\text{gas}}} + \frac{1 - \varepsilon}{3k_{gr}} \tag{12}\]

where \(k_{gr}\) and \(k_{\text{gas}}\) are the thermal conductivities of the graphite solid matrix and of the gas mixture, respectively. The energy transport equation for the gas diffusers, in non-dimensional form will be therefore (14):

\[
\frac{1}{q_x} \frac{\partial T}{\partial x} + \frac{1}{q_y} \frac{\partial T}{\partial y} = \frac{1}{\text{RePr}} \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right) \tag{13}\]

where

\[
\text{Pr} = \frac{c_p \mu}{k_{\text{eff}}} \]

c\(_p\) standing for the specific heat of the gas mixture at constant pressure. The variables in equation (13) have been non-dimensionalised in the same manner like equation (4) and is similar to it.

The chemical species in the gas mixtures will be transported by diffusion and locally by convection. The effective macroscopic diffusion coefficient for the \(k'\) th component in the frame of the adopted schematical porous medium model will be (14):

Electrochemical Society Proceedings Volume 98-27
\[ D_{eff,k} = \frac{3\varepsilon - 1}{2\varepsilon} D_k \quad \text{if} \quad \varepsilon > 1/3 \]
\[ D_{eff,k} = 0. \quad \text{if} \quad \varepsilon \leq 1/3 \]  

where \( D_k \) is the microscopic diffusion coefficient for the \( k \) th species, defined by equation [6]. The transport equation for the chemical species in nondimensional form will become:

\[
\begin{align*}
 q_x \frac{\partial X_k}{\partial x} + q_y \frac{\partial X_k}{\partial y} &= \frac{\varepsilon}{Re Sc_k} \left( \frac{\partial^2 X_k}{\partial x^2} + \frac{\partial^2 X_k}{\partial y^2} \right) \\
\end{align*}
\]

where Schmidt number is defined in terms of the effective macroscopic diffusion coefficient given by equation [14]:

\[ Sc_k = \frac{\mu}{\rho D_{eff,k}} \]

Equation [15] is non-dimensionalised in the same manner like equation [5] and is similar to it.

In Membrane

The subject of the transport equations in the porous membrane are variables related to the water flow; therefore, similar equations like the ones developed for the gas diffusers may apply, if the proper parameters for water are plugged in. A different form of the momentum transport equations, containing source terms accounting for electro-osmotic forces has to be used here. In non-dimensional form, these equations read:

\[
\begin{align*}
 \bar{q}_x \frac{\partial \bar{q}_x}{\partial \bar{x}} + \bar{q}_y \frac{\partial \bar{q}_y}{\partial \bar{y}} &= -\varepsilon \frac{\partial P}{\partial \bar{x}} + \frac{1}{Re} \left( \frac{\partial^2 \bar{q}_x}{\partial \bar{x}^2} + \frac{\partial^2 \bar{q}_y}{\partial \bar{y}^2} \right) - \varepsilon \frac{\mu}{k_p} \frac{q_x}{\rho U_i} D + \\
&+ \frac{k_p c_f}{k_p} \frac{1}{\bar{x}} \frac{\partial \bar{q}_x}{\partial \bar{x}} \frac{1}{\rho U_i^2 L} \end{align*}
\]

Electrochemical Society Proceedings Volume 98-27 495
Equations [16] and [17] represent a generalized form of the Schlögl’s equations.

The transport of the dissolved protons is governed by an equation similar to equation [15], with an extra term accounting for migration:

\[
\frac{-q_x}{q_x} \frac{\partial X_{H^+}}{\partial x} + \frac{q_y}{q_y} \frac{\partial X_{H^+}}{\partial y} = \frac{\varepsilon_m}{Re S c_{H^+}} \left( \frac{\partial^2 X_{H^+}}{\partial x^2} + \frac{\partial^2 X_{H^+}}{\partial y^2} \right) + \varepsilon_m^2 X_{H^+} F_D \frac{D_{eff,H^+}}{RT} \left( \frac{\partial \phi}{\partial x} + \frac{\partial \phi}{\partial y} \right) \frac{1}{U_i L} \]

The energy equation is similar to equation [13] with a new ohmic source term:

\[
-\frac{q_x}{q_x} \frac{\partial \bar{T}}{\partial x} + \frac{q_y}{q_y} \frac{\partial \bar{T}}{\partial y} = \frac{1}{Re Pr} \left( \frac{\partial^2 \bar{T}}{\partial x^2} + \frac{\partial^2 \bar{T}}{\partial y^2} \right) + \frac{i^2}{\sigma_m U_i \rho_i c_i T_i} \]

and the effective conductivity given by equation [14], with \(k_{gr}^m\) replaced by \(k_{m, dry}^m\) and \(k_{gas}^m\) by \(k_{m, l}^m\). In equation [19], \(i\) is the modules of the membrane phase current density vector and \(\sigma_m\) is the ionic conductivity.

For the membrane phase potential the following equation applies:

\[
\frac{\partial}{\partial x} \left( \sigma_m \frac{\partial \Phi}{\partial x} \right) + \frac{\partial}{\partial y} \left( \sigma_m \frac{\partial \Phi}{\partial y} \right) = 0. \]

and the membrane phase current density satisfies:

Electrochemical Society Proceedings Volume 98-27
\[ i_x = -\sigma_n \frac{\partial \phi}{\partial x} - F z_x e_x u \]  

\[ i_y = -\sigma_n \frac{\partial \phi}{\partial y} - F z_x e_y v \]  \hspace{1cm} \text{[21]} 

\textbf{In Catalyst Layers}

Continuity and equations [16] and [17] apply in these regions with the porosity \( \varepsilon_m \) replaced by \( \varepsilon_{m\text{em}} \), where \( \varepsilon_{m\text{em}} \) is the membrane volume fraction in the catalyst layer. Equations like [15] will apply, with the following source terms:

- at the anode, the source term for the hydrogen molecules and hydrogen protons are:

\[ -\frac{1}{2F} j_a \frac{D}{U_c} \text{ and } \frac{1}{F} j_a \frac{L}{U_c} \]  \hspace{1cm} \text{[22]} 

- At the cathode side, the source terms for the oxygen, water and hydrogen protons are:

\[ -\frac{1}{4F} j_c \frac{D}{U_c}, \frac{1}{2F} j_c \frac{L}{U_c} \text{ and } -\frac{1}{F} j_c \frac{L}{U_c} \]  \hspace{1cm} \text{[23]} 

where the transfer current \( j_a \) and \( j_c \) are defined by the Butler-Volmer expressions:

\[ j_a = \alpha_j \text{ref} \left( \frac{X_{H_2}}{X_{H_2\text{ref}}} \right)^{\frac{1}{2}} \left[ e^{\frac{\alpha_j F}{RT}} - \frac{1}{e^{\frac{\alpha_j F}{RT}}} \right] \]  \hspace{1cm} \text{[24]} 

\[ j_c = \alpha_j \text{ref} \left( \frac{X_{O_2}}{X_{O_2\text{ref}}} \right) \left[ e^{\frac{\alpha_j F}{RT}} - \frac{1}{e^{\frac{\alpha_j F}{RT}}} \right] \]  \hspace{1cm} \text{[25]} 

Equation [13] applies with the a new source term:
\[
\frac{\partial T}{\partial x} + q_y \frac{\partial T}{\partial y} = \frac{1}{\text{Re} \, \text{Pr}} \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right) + i \eta \frac{D}{U, \rho, \varepsilon, \sigma_i, T, D_{el}} [26]
\]

The membrane phase potential satisfies equation:

\[
\frac{\partial}{\partial x} \left( \sigma_m \frac{\partial \Phi}{\partial x} \right) + \frac{\partial}{\partial y} \left( \sigma_m \frac{\partial \Phi}{\partial y} \right) = -j_e \quad \text{at anode} [27]
\]

\[
\frac{\partial}{\partial x} \left( \sigma_m \frac{\partial \Phi}{\partial x} \right) + \frac{\partial}{\partial y} \left( \sigma_m \frac{\partial \Phi}{\partial y} \right) = -j_e \quad \text{at cathode}
\]

The membrane phase current density satisfies:

\[
\frac{\partial q_x}{\partial x} + \frac{\partial q_y}{\partial y} = j_e \quad \text{at anode} [28]
\]

\[
\frac{\partial q_x}{\partial x} + \frac{\partial q_y}{\partial y} = j_e \quad \text{at cathode}
\]

The next additional equations have to be as well part of the system:

- the equation of state for the perfect gasses apply in the first and third domains of Fig. 2:

\[
\frac{p}{\rho} = RT [29]
\]

- the ionic conductivity of the membrane has the following expression:

\[
\sigma_m = \frac{F_i^+}{RT} D_{\sigma_i} c_{H^+} z_{H^+} [30]
\]
It has been shown anyhow that the membrane ionic conductivity is not only a function of
temperature, but it features a strong dependence on the membrane water content. Springer
et al. (6) present the following empirical expressions to determine the ionic conductivity in
a 117 Nafion® proton exchange membrane:

\[ \sigma_{ref}^* = 0.005139 \lambda - 0.00326 \quad \text{if } \lambda \geq 1 \quad [31] \]

where \( \sigma_{ref}^* \) is the reference ionic conductivity at a temperature of 303 K. For values of the
membrane water content with \( \lambda \) less than one, the reference ionic conductivity is assumed
constant. At other temperatures, it is given by:

\[ k(T) = \sigma_{ref}^* \exp \left[ 1268 \left( \frac{1}{303} - \frac{1}{T} \right) \right] \quad [32] \]

where temperature is expressed in K. The membrane water content in equation [31] is
given by the following empirical formula (6):

\[ \lambda = 0.043 + 17.81a - 39.85a^2 + 36.0a^3 \quad \text{for } 0 < a \leq 1 \]
\[ \lambda = 14 + 1.4(a-1) \quad \text{for } 1 \leq a \leq 3 \quad [33] \]

\( a \) being the water vapor activity at the cathode gas diffuser-catalyst layer interface
assuming equilibrium, given by:

\[ a = \frac{X_{v}P}{P_{sat}} \quad [34] \]

The saturated water partial pressure is expressed by the following empirical equation
that fits the tabulated values (6):

\[ \log_{10} P_{sat} = -2.1794 + 0.029537 \cdot 10^{-3} T^2 - 9.1837 \cdot 10^{-5} T^3 + 1.4454 \cdot 10^{-7} T^3 \quad [35] \]
the temperature dependence of the binary diffusion coefficients is given by Slattery and Bird (16):

\[ pD_{A,B} = a \left( \frac{T}{T_{oA}T_{oB}} \right)^b \left( \frac{1}{M_A} + \frac{1}{M_B} \right)^{1/2} \left( \frac{P_{oA}P_{oB}}{T_{oA}T_{oB}} \right)^{1/2} \]  \[36\]

where \( a \) and \( b \) are constants, the pressure is in bar, and the binary diffusion coefficient in \( \text{cm}^2\cdot\text{s}^{-1} \).

- the thermodynamic open circuit potential for the overall reaction is given by (5):

\[ E = 1.23 - 0.9 \cdot 10^{-3}(T-298) + 2.3 \frac{RT}{4F} \log\left( \frac{P_{H_2}^2}{P_{O_2}} \right) \]  \[37\]

Examination of equation [37] shows a decrease of the open circuit potential with temperature. Experimental results show an opposite effect. This is due to higher exchange current density for oxygen reduction at higher temperatures (17). At the time being, we are not aware of any mathematical model to describe this dependency, therefore we used the empirical results of Parthasarathy et al. (17) in our formulation. They tabulated values for the open circuit potential as a function of temperature, which can be fitted in the following equation:

\[ E = 0.0025T + 0.2329 \]  \[38\]

temperature being in \( K \).

The special treatment of the boundary conditions and the solution technique are presented in detail elsewhere (12).
NOMENCLATURE

\(a\)  
water vapor activity

\(a_{j_o}^{ref}\)  
reference exchange current density times area, \(A.m^{-2}\)

\(c\)  
molar concentration, \(mol.m^{-3}\)

\(c_f\)  
concentration of the sulfonic ions, \(mol.m^{-3}\)

\(c_p\)  
specific heat, \(J.kg^{-1}K^{-1}\)

\(D\)  
gas channel width, \(m\)

\(D_{cl}\)  
catalyst layer thickness, \(m\)

\(D_k\)  
diffusion coefficient of the k'th component, \(m^2.s^{-1}\)

\(F\)  
Faraday constant, 96,487 \(C/mol\)

\(E\)  
Thermodynamic open circuit potential, \(V\)

\(i\)  
current density, \(A.m^{-2}\)

\(I_{avg}\)  
operating cell current density, \(A.m^{-2}\)

\(j\)  
transfer current, \(A.m^{-3}\)

\(k\)  
permeability of gas in the porous layer, \(m^2\)

\(k\)  
thermal conductivity, \(W.m^{-1}.K^{-1}\)

\(k_p\)  
hydraulic permeability of the porous layer, \(m^2\)

\(k_e\)  
electrokinetic permeability, \(m^2\)

\(L\)  
membrane width, \(m\)

\(M\)  
molecular mass, \(kg.kmol^{-1}\)

\(n\)  
umber of electrons participating in reaction

\(p\)  
pressure, \(Pa\)

\(Pr\)  
Prandtl number

\(q\)  
specific discharge, \(m.s^{-1}\)

\(Q\)  
heat source, \(W.m^{-2}\)

\(R\)  
resistance, \(\Omega\)

\(R\)  
universal gas constant, 8,314 \(J.mol^{-1}.K^{-1}\)

\(r^{(20)}\)  
coefficient.

\(Re\)  
Reynolds number

\(S\)  
entropy, \(J.kg^{-1}.K^{-1}\)

\(S\)  
source term of the generalised transport equation

\(Sc\)  
Schmidt number

\(T\)  
temperature, \(K\)

\(u, v\)  
velocity components, \(m.s^{-1}\)

\(U_i\)  
inlet velocity, \(m.s^{-1}\)

\(x, y\)  
coordinates, \(m\)

\(X\)  
mole fraction

\(z_f\)  
charge number of the sulfonic ions
Greek Symbols

\( \alpha \)  transfer coefficient
\( \Gamma \)  diffusion coefficient of the generalised transport equation
\( \varepsilon \)  porosity
\( \eta \)  total electrode overpotential, \( V \)
\( \lambda \)  membrane water content, \( mol H_2O / mol SO_3 \)
\( \rho \)  density, \( kg.m^{-3} \)
\( \mu \)  viscosity, \( kg.m^{-1}.s^{-1} \)
\( \phi \)  membrane phase potential, \( V \)
\( \sigma_m \)  membrane ionic conductivity, \( \Omega.m^{-1} \)
\( \xi \)  stoichiometric ratio

Superscripts

-  nondimensionalised variable
\( \rightarrow \)  vector
\( \text{ref} \)  reference

Subscripts

\( a \)  anode
\( A, B \)  components
\( \text{avg} \)  average
\( c \)  cathode
\( ch \)  channel
\( cl \)  catalyst layer
\( cr \)  critic
\( e \)  exit
\( \text{eff} \)  effective
\( f \)  related to the sulfonic acid ions
\( \text{gas} \)  related to the gas mixture
\( gr \)  related to the graphite
\( H^+ \)  related to the hydrogen protons
\( H_2 \)  related to the hydrogen molecule
\( i \)  inlet
\( k \)  \( k'th \) component
\( l \)  liquid
\( m \)  related to the membrane
\( mc \)  membrane volume in catalyst layer
\( O_2 \)  related to the oxygen molecule
\( pm \)  porous medium
$w$ wall or related to water
$x, y$ directions
$+$ cathode

REFERENCES

13. S. Kakac, Y. Yener, Convective Heat Transfer. Second edition, CRC Press (1994)
14. G. Dagan, Flow and Transport in Porous Formations, Springer-Verlag (1989)
15. G. Dagan, Water Resources Research, 15, 1 (1979)
16. J. C. Slattery, R. B. Bird, AIChE J., 137 (1958)
17. A. Parthasarathy, S. Srinivasan, A. J. Appleby, J. Electrochem. Soc., 139, 2530 (1992)