Mathematical Model of Gas Transport in Anisotropic Porous Electrode of the PEM Fuel Cell

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Abstract. In this paper a gas mixture model is developed to study anisotropic hydrogen and water vapour flow in anode of the PEM fuel cell. Dependence of the distribution of concentrations and fluxes of the of gas components in anisotropic porous layer is investigated. First full partial differential equations describing mass transport for permeability and diffusivity tensors based on Darcy's and Fick's laws are developed. Next this set of nonlinear equations together with appropriate nonlinear boundary conditions using finite element method was solved. At the end an illustrative example is given.

1 Introduction

The Proton Exchange Membrane (PEM) fuel cell consists of two gas diffusion layers (GDL) separated by PEM. Between each GDL and PEM thin platinum catalyst layer is located. Numerical simulation of all aspects of GDL performance is very important from practical point of view because, most of the working parameters is very difficult to measure. This is caused mainly by small physical dimensions of single cell. Typical cell electrodes are made of carbon fibre paper, consists of single carbon fibres. Because of this, GDL diffusion and convection coefficients are not constant numbers but tensor values.

One of the first publication on simulation of the PEM fuel cell based on the fluid flow approach, started after publication [1]. In this publication authors described equations governing gas distribution in one dimension in different regions of membrane-electrode assembly, the transport of mass species inside GDL and electrochemical reactions. We decouple GDL from the rest of the assembly by appropriate boundary conditions, occurring in the gas channel and on the catalyst layer.

Anisotropic properties of the GDL were investigated by many authors, but few publications with numerical models of anisotropic fuel cell were presented. In [2] authors simulate gas distribution in anisotropic porous electrodes but they do not show full equations which flow fields should fulfil. In this article authors present full equations describing gas distribution in anode of the PEM fuel cell and extend results presented in [2] to the full anisotropic case, where anisotropic properties of the material are described by full permeability and diffusivity tensors. At the end some illustrative example is given.

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2 Numerical Model of the Anisotropic Electrode

At the Fig. 1 cross section of the anode of the PEM fuel cell is shown. Gas mixture is supplied by the inlet flow channel and distributed to the electrochemical reaction sites by the anisotropic porous layer. At the PEM electrolyte boundary, where very thin catalyst layer is present, hydrogen molecules H_2 are split into hydrogen ions H^+ and free electrons in electrochemical reaction. The hydrogen ions flow farther in direction of the cathode and electrons flow back to the interdigitated graphite plate, where graphite is carrying them out to the external load. Through the polymer electrolyte from the cathodic side to the anode-electrolyte boundary, water molecules are transported. In this publication we assume that temperature of the fuel cell is high enough for all this water to evaporate. Thus, it is further assumed that water occurs only as a vapour.

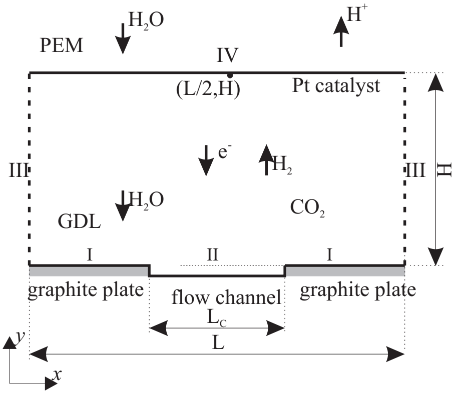

Fig. 1. Cross section of the PEM anode together with geometrical dimensions.

For practical reasons the hydrogen is obtained from hydrocarbons after catalytic reforming process. As a result in the gas mixture, with which cell is supplied, carbon dioxide is present. It is an inert gas but influences distribution of hydrogen and water vapour distribution, it should be taken into account during calculations.

Mass transport of the reactant gases obeys two fundamental laws, namely Darcy's and Fick's laws. The first law defines convection flow which is proportional to the pressure difference and the second diffusion flow which depends on concentration gradients. Both laws are correct for homogeneous and isotropic mediums, described by constant coefficients.

3 Mathematical Model of the Anisotropic Porous Layer

The overall flow of the gas mixture $\mathbf{N} = C\mathbf{U}$ is governed by the mass conservation law which in our case can be written in the form

$$\nabla(C\mathbf{U}) = 0 \tag{1}$$

where $\mathbf{U}$ is a gas molar average velocity and C is a gas mixture concentration. It is a sum of the concentration of all three species: $C = C_1 + C_2 + C_3$, where C_1 is concentration of hydrogen, C_2 is concentration of water vapour and C_3 is concentration of carbon dioxide. We assume further that CO_2 concentration is a fixed part of the mixture concentration C, and is equal $(1 - \gamma_r)C$. Molar average velocity is described by Darcy's law:

$$\mathbf{U} = -\frac{1}{\varepsilon_0 \mu} \bar{\bar{K}} \nabla P \tag{2}$$

where $\bar{\bar{K}}$ is a permeability tensor given by a matrix

$$\mathbf{K} = \begin{bmatrix} k_{11} & k_{12} \\ k_{21} & k_{22} \end{bmatrix} \tag{3}$$

Ideal gas law relates pressure with the gas mixture concentration C

$$P = CRT \tag{4}$$

Taking into account above relation and defining convection matrix $\mathbf{\Gamma}$ as

$$\mathbf{\Gamma} = \begin{bmatrix} \gamma_{11} & \gamma_{12} \\ \gamma_{21} & \gamma_{22} \end{bmatrix} = \frac{RT}{\varepsilon_p \mu} \mathbf{K} \tag{5}$$

the Darcy's Law can be formulated for the anisotropic case as

$$\begin{bmatrix} U_x \\ U_y \end{bmatrix} = -\begin{bmatrix} \gamma_{11} & \gamma_{12} \\ \gamma_{21} & \gamma_{22} \end{bmatrix} \begin{bmatrix} \dfrac{\partial C}{\partial x} \\ \dfrac{\partial C}{\partial y} \end{bmatrix} \tag{6}$$

Introducing (6) into (1) we get the first partial differential equations governing the process of mass transport in the electrode

$$-\gamma_{11} \frac{\partial}{\partial x}\left(C \frac{\partial C}{\partial x} \right) - \gamma_{12} \frac{\partial}{\partial x}\left(C \frac{\partial C}{\partial y} \right) - \gamma_{21} \frac{\partial}{\partial y}\left(C \frac{\partial C}{\partial x} \right) - \gamma_{22} \frac{\partial}{\partial y}\left(C \frac{\partial C}{\partial y} \right) = 0 \tag{7}$$

Also hydrogen flux $\mathbf{N}_1 = C_1 \mathbf{U}_1$ has to fulfil mass conservation law:

$$\nabla \mathbf{N}_1 = 0 \tag{8}$$

Hydrogen flux consists of two parts: convective flux $C_1\mathbf{U}$ and diffusive flux $\mathbf{J}_1$:

$$\mathbf{N}_1 = C_1 \mathbf{U} + \mathbf{J}_1 \tag{9}$$

Convective flux is related with concentration gradients by Fick's law:

$$\mathbf{J}_1 = -C\overline{\overline{D}}\nabla x_1 \tag{10}$$

where tensor $\overline{\overline{D}}$ is given by matrix

$$\mathbf{D} = \begin{bmatrix} d_{11} & d_{12} \\ d_{21} & d_{22} \end{bmatrix} \tag{11}$$

Thus Fick's law for anisotropic case has following form:

$$\begin{bmatrix} J_{1x} \\ J_{1y} \end{bmatrix} = -C \begin{bmatrix} d_{11} & d_{12} \\ d_{21} & d_{22} \end{bmatrix} \begin{bmatrix} \dfrac{\partial x_1}{\partial x} \\ \dfrac{\partial x_1}{\partial y} \end{bmatrix} \tag{12}$$

Introducing equations (6) and (12) into (8) we get and eliminating C_1 by introducing C_1=x_1C we get second partial differential equation describing mass transport in anode of the PEM fuel cell:

$$\begin{aligned} &-d_{11}\frac{\partial}{\partial x}\left(C\frac{\partial x_1}{\partial x}\right) - d_{12}\frac{\partial}{\partial x}\left(C\frac{\partial x_1}{\partial y}\right) - d_{21}\frac{\partial}{\partial y}\left(C\frac{\partial x_1}{\partial x}\right) - d_{22}\frac{\partial}{\partial y}\left(C\frac{\partial x_1}{\partial y}\right) - \\ &-C\left(\gamma_{11}\frac{\partial x_1}{\partial x}\frac{\partial C}{\partial x} + \gamma_{12}\frac{\partial x_1}{\partial x}\frac{\partial C}{\partial y} + \gamma_{21}\frac{\partial x_1}{\partial y}\frac{\partial C}{\partial x} + \gamma_{22}\frac{\partial x_1}{\partial y}\frac{\partial C}{\partial y}\right) = 0 \end{aligned} \tag{13}$$

Equations (7) and (13) form complete set of equation in total mixture concentration C and molar fraction of hydrogen x_1 variables.

4 Boundary Conditions

Equations (7) and (13) have to fulfil adequate boundary conditions. Each of them needs different types of Dirichlet's and Neuman's conditions for four dinstinct boundary sections.

Section I – Graphite Plate

Along this part of boundary graphite plate contacts with carbon fibre material and throughout this section can be no flux of any species. Because fluxes of all species at this boundary section are parallel to the boundary surface, the fluxes entering the graphite plate are equal zero.

$$\frac{\partial x_1}{\partial n} = 0 \quad \text{and} \quad \frac{\partial C}{\partial n} = 0 \tag{14}$$

Section II –Inlet Flow Channel

On this part of the boundary fibrous carbon material contacts with flow channel and reactant species enter the anode. This results following Dirichlet's conditions:

$$C = C_{\mathrm{g}} \quad \text{and} \quad x_1 = x_{1\mathrm{g}} \tag{15}$$

where C_{g} is given molar concentration of mixture and $x_{1\mathrm{g}}$ given molar fraction of hydrogen in inlet channel.

Section III – Left and Right Sides of the Calculation Domain

We assume that solution is periodic with respect to the calculation variables, and thus all fluxes are directed parallel to the y axis. This causes that boundary conditions in this section are the same as for section I.

Section IV – Platinum Catalyst Layer

Gas diffusion layer contacts with catalytic material along this part of the boundary. Here hydrogen atoms lose their electrons during electrochemical reaction. Those electrons flow back to graphite plate and next through external circuitry to the cathode. Hydrogen ions flow further through proton membrane. Here hydrogen flux crossing boundary is proportional to its molar concentration difference on both sides of boundary. We assume that electrochemical reaction efficiency is equal 100% and no hydrogen atoms enter proton membrane. Thus

$$\mathbf{N}_1 \cdot \mathbf{n} = N_1^{\mathrm{n}} = r_H \left(C_1 - C_{1\mathrm{out}}\right) = r_H \left(C_1 - 0\right) = r_H C_1 \tag{16}$$

where the mass transfer coefficient r_H models electrochemical reaction which takes place in catalyst layer. It relates hydrogen flux with its molar concentration and can be determined from averaged current density flowing throughout catalytic region.

The water in fuel cell is produced on the cathode side of the membrane and its majority is transported from this region to cathodic gas channel. However, some part of water diffuses throughout membrane to anode, crosses anodic catalytic layer and enters anode. This flux of water vapour is strictly related to hydrogen flux flowing in opposite direction, because from every two hydrogen atoms one water molecule is produced. This relation between hydrogen flux and water vapour flux is established by return coefficient v which determines direction and magnitude water vapour flux $\mathbf{N}_2$:

$$\mathbf{N}_2 \cdot \mathbf{n} = \left(\nu - 1\right) \mathbf{N}_1 \cdot \mathbf{n} = \left(\nu - 1\right) r_h C x_1 \tag{17}$$

Equations (16) and (17) are starting points for derivation Neuman's boundary conditions on catalyst layer for molar mixture concentration C and molar hydrogen fraction x_1. From (16) we get:

$$x_1 \gamma_{21} \frac{\partial C}{\partial x} + x_1 \gamma_{22} \frac{\partial C}{\partial y} + d_{21} \frac{\partial x_1}{\partial x} + d_{22} \frac{\partial x_1}{\partial y} = -r_h x_1 \tag{18}$$

Carrying out the same manipulations as for hydrogen from (17) we get relation between partial normal derivative for hydrogen and mixture concentration

$$(\gamma_r - x_1)\gamma_{21}\frac{\partial C}{\partial x} + (\gamma_r - x_1)\gamma_{22}\frac{\partial C}{\partial y} - d_{21}\frac{\partial x_1}{\partial x} - d_{22}\frac{\partial x_1}{\partial y} = -(\nu - 1) r_h x_1 \tag{19}$$

It is reasonable to assume that fluxes on this boundary enter catalyst layer perpendicularly and that no tangential fluxes are present. This means that partial derivatives of all calculation variables in directions tangential to the boundary are equal zero, thus, after simplification and solving system of equations, we get Neuman's boundary conditions for C and x_1 variables:

$$\frac{\partial C}{\partial y} = -\frac{\nu r_h x_1}{\gamma_r \gamma_{22}} \quad \text{and} \quad \frac{\partial x_1}{\partial y} = \frac{r_h x_1 (\nu x_1 - \gamma_r)}{d_{22}\gamma_r} \tag{20}$$

5 An Illustrative Example

The geometry of numerical example are defined in fig.1.Numerical values was presented in [3] and will not be repeated here.
Let us assume further that main axes of anisotropy overlap with geometrical coordinates. This results in following form of anisotropy for convective and diffusive matrixes

$$\mathbf{\Gamma} = \Gamma\begin{bmatrix} \chi_g & 0 \\ 0 & 1 \end{bmatrix} \text{and } \mathbf{D} = D\begin{bmatrix} \chi_d & 0 \\ 0 & 1 \end{bmatrix} \tag{21}$$

Let us further assume that both anisotropic ratios are equal $\chi_g = \chi_d = \chi$. For this simplified assumptions equations (7) and (13) will take following form:

$$\chi\frac{\partial}{\partial x}\left(C\frac{\partial C}{\partial x}\right) + \frac{\partial}{\partial y}\left(C\frac{\partial C}{\partial y}\right) = 0 \tag{22}$$

$$\chi\frac{\partial}{\partial x}\left(C\frac{\partial x_1}{\partial x}\right) + \frac{\partial}{\partial y}\left(C\frac{\partial x_1}{\partial y}\right) + \frac{C\Gamma}{D}\left(\chi\frac{\partial x_1}{\partial x}\frac{\partial C}{\partial x} + \frac{\partial x_1}{\partial y}\frac{\partial C}{\partial y}\right) = 0 \tag{23}$$

For anisotropic ratio $\chi = 1$ the above equations reduce to the usual equations for isotropic and homogeneous case [4]. The above set of mutually coupled and nonlinear equations was solved in two dimensions by finite element method.

The dependencies between fluxes of species and anisotropy ratio were investigated during the calculations. The calculations were carried out at point (L/2,H) in the middle of top domain boundary, across the GDL at y=H/2. In the fig. 2 and 3 the total flux of the hydrogen is shown for two highly different anisotropy ratios. We can see differences between directions of the fluxes caused by difference in anisotropic ratio of carbon fibres assumed for each calculation. In the figures 4 and 5 dependence between anisotropic ratio and diffusion flux of hydrogen is shown. For anisotropy ratio $\chi = 1$, the numerical results are consistent with general equations [5].

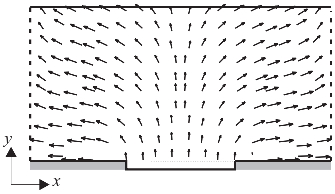

Fig. 2. Total flux of hydrogen $\mathbf{N}_1$ for anisotropic ratio $\chi = 0.2$.

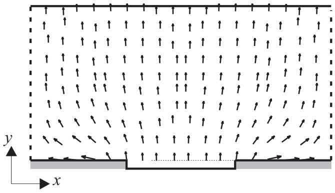

Fig. 3. Total flux of hydrogen $\mathbf{N}_1$ for anisotropic ratio $\chi = 1.8$.

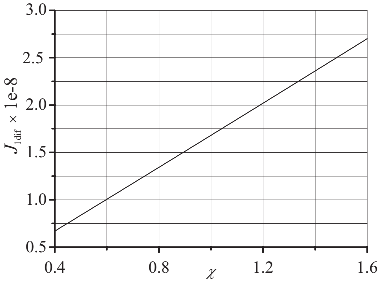

Fig. 4. Dependence between diffusion modulus of the flux of hydrogen J_{1diff} and anisotropic ratio χ at point, placed on middle point of the catalytic layer (L/2, H).

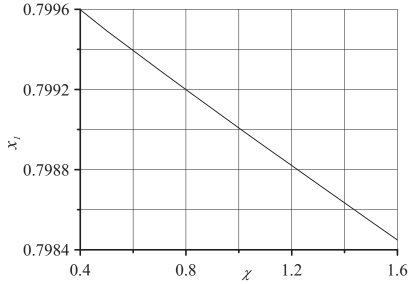

Fig. 5. Dependence between molar fraction of hydrogen x_1 and anisotropic ratio χ at calculation point, placed on middle point of the catalytic layer (L/2, H).

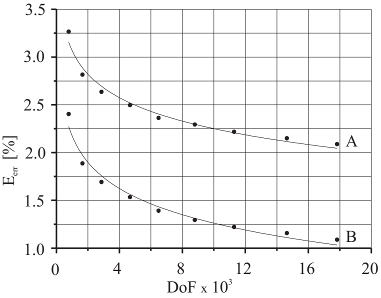

Fig. 6. Dependency between DoF and E_{err} coefficient for normal components of the water vapour flux $\mathbf{N}_2$ (A) and hydrogen flux $\mathbf{N}_1$ (B).

In Fig. 4, dependence of modulus of the hydrogen diffusion flux is presented. In the middle of catalytic layer for $\chi < 1$ less hydrogen reaches middle parts of the cathode-electrolyte boundary. This means that distribution of hydrogen on the catalyst layer is more uniform. This in turn results in greater effectiveness of the electrochemical reaction of the splitting hydrogen molecules into hydrogen ions and electrons, what gives greater electric cell performance. It is obvious that there exists an optimal value of the anisotropic ratio for which electrochemical reaction effectiveness on this electrode attains maximal value. To calculate this optimal value of χ one has to use any optimization method. In this publication this problem will be not further considered.

Convergence of the solution of the problem was investigated by analysing dependence between error coefficient E_{err} defined by (24) and degrees of freedom (DoF) of discretized form of problem equations. Analyse was done for normal component of fluxes of each gas component $\mathbf{N}_1$ and $\mathbf{N}_2$. Results of this investigation are shown in fig. 6. We can see, that increasing of DoF decreases percentage error coefficient, what means, that problem is convergent.

$$E_{err} = \frac{\oint_L \mathbf{N}_i \cdot d\mathbf{l}}{\oint_L \left|\mathbf{N}_i \cdot \mathbf{n}\right| \cdot d\mathbf{l}} 100\% \tag{24}$$

where $i = 1$ or 2.

6 Conclusions

In this paper we present a mathematical model of multicomponent gas transport in the GDL, which includes the full anisotropy of porous material. We assumed that anisotropy tensors for both convective and diffusive fluxes for hydrogen and water vapour are equal each to other. Generally it is not the case. Further work should be carried to take into account pressure as the third independent variable, and to include physical aspects of anisotropic coefficients and their mutual relation.

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