September 10 - 12, 2003

Pilsen, Czech Republic

GAS COMPONENTS TRANSPORT IN THE INHOMOGENEOUS CATHODE OF PEM FUEL CELL

PROF. NZ. DR HAB. INŻ. EUGENIUSZ KURGAN[1]
MGR INŻ. PAWEŁ SCHMIDT.[2]

Abstract: In practical operation of the fuel cell both hydrogen and oxygen can contain some pollute particles as dust, carbon molecules or condensed water droplets. These particles can be together with gas mixture transported to gas diffusion layer where they settle down and clog electrode pores. These results in decreasing layer gas permeability and in effect also gas mixture flow. The deposition of these pollute particles is not distributed uniformly over whole electrode but instead concentrates in region, where gas mixture flows into electrode. This results in inhomogeneous distribution of layer permeability. Field equations for this case are formulated and next solved by finite element method.

Keywords: Inhomogeneous fuel cells, gas species transport, finite element method.

1 Introduction

One of the ways to understand an operation of fuel cells is to treat of them as a sort of the ordinary battery. Both devices produce electricity through electrochemical reactions. The difference between them consists in that a fuel cell can constantly produce electricity as long as it has a source of fuel whereas a battery needs to be recharged. One of the most crucial issues is gas mixture transport to and from electrochemical reaction sites. Inhomogeneity of the material from whom which diffusion layer is made is an important factor in overall fuel efficiency. It directly influences the porosity factor of the porous material and through this gas transport velocity [1]. Mutual relation between inhomogeneity of the porous material and gas components flow distribution is investigated. At the end some illustrative example is given.

2 Main equations

Fuel cells have essentially higher efficient coefficient as many other energy sources, but permanent progress is required to increase power efficiency, current density and to reduce cost of manufacturing [2]. There are three different critical transport phenomena in PEM fuel cell, which have influence on these factors: (a) heat transport problems, (b) water and water vapour management and (c) mass transport limitations. In this article we focus ourselves onto calculation of gas component transport in cathode but with regard to material inhomogeneity.

The total gas concentration is denoted by C and is equal:

$$C = C_1 + C_2 + C_3 \tag{1}$$

where oxygen has concentration C_1, water vapor has molar concentration C_2 and CO_2 has concentration C_3. We assume further that nitrogen concentration is a fixed part of the total concentration C which is equal $(1 - \gamma_r)C$, thus $C = C_1 + C_2 + (1 - \gamma_r)C$ [3]. As unknown variables we assume total concentration C and oxygen fracture $x_1 = C_1/C$. The conservation of mass for the gas mixture is in steady state given by:

$$\nabla \cdot (C \mathbf{U}) = 0 \tag{2}$$

Velocities of individual components differ significantly because of intercomponent diffusion. Every mixture component also has to fulfill mass conservation low, where $\mathbf{J}_i$ is the diffusive flux measured relative to the molar averaged velocity $\mathbf{U}$. The total convective and diffusive flux of this component with respect to static or laboratory coordinates takes the form [4]

$$\mathbf{N}_1 = C_1 \mathbf{U}_1 = C_1 \mathbf{U} + \mathbf{J}_1 \tag{3}$$

The diffusive flux of any gaseous component $\mathbf{J}_i$ is given by Fick's law, which states that molar flux of this component is relative to the molar-averaged velocity is proportional to the gradient of the mole fraction C_i/C according with relation:

$$\mathbf{J}_1 = C_1 (\mathbf{U}_1 - \mathbf{U}) = -DC\nabla\left(\frac{C_1}{C}\right) = -DC\nabla x_1 \tag{4}$$

where coefficient D is the diffusivity. Assuming inhomogeneous behaviour of porous material we get

$$\mathbf{U} = -\frac{K}{\varepsilon_p \mu}\nabla(P) = -\frac{K}{\varepsilon_p \mu}\nabla(RTC) = -\Gamma\nabla C \tag{5}$$

where coefficient Γ is special dependent and is given by following phenomenological relation [5,6]:

$$\Gamma(x,y) = 4\Gamma_0 \left[0.25 + K_1 \left(0.995 \left(0.00001 + \frac{y}{H} \right)^{0.05} - 1 \right) e^{-K_3(x-0.5L)^8} - \right.$$
$$\left. - K_4 \left(\left(0.00001 + \frac{y}{H} \right)^{0.6} - 1 \right) e^{-K_6(x-0.5L)^2} \right] \tag{6}$$

where $K_1 = 0.6$, $K_3 = 3000$, $K_4 = 0.08K_1$, $K_6 = 20$. Changing coefficient K_1 we can simulate the process of pollution of the porous material at the inlet of the electrode. The total flux $\mathbf{N}$ is a sum of fluxes of all three components:

$$\mathbf{N} = \sum_i \mathbf{N}_i = \sum_i C_i \mathbf{U}_i = C \left(\frac{1}{C} \sum_i C_i \mathbf{U}_i \right) = C\mathbf{U} \tag{7}$$

Utilizing mass conservation law we get:

$$\nabla \cdot (\Gamma C \nabla C) = 0 \tag{8}$$

This is the first partial differential equation for C variable. The second one can be derived from the molar conservation law for oxygen $\nabla \cdot \mathbf{N}_1 = 0$, where molar flux of the oxygen $\mathbf{N}_1$ relative to the laboratory-fixed coordinate reference system is given by $\mathbf{N}_1 = C_1 \mathbf{U} + \mathbf{J}_1$. The oxygen flux $\mathbf{N}_1$ can be calculated as:

$$\mathbf{N}_1 = -\Gamma C_1 \nabla C - D_1 C \nabla(x_1) \tag{9}$$

Mass conservation law for oxygen flux $\mathbf{N}_1$ gives the desired second equation:

$$\nabla \cdot \mathbf{N}_1 = \nabla \cdot \left[-\Gamma C_1 \nabla C - D_1 C \nabla(x_1) \right] = 0 \tag{10}$$

This equation can be further simplified to the form:

$$\nabla \cdot \left[D_1 C \nabla(x_1) \right] + \Gamma(x,y) C \nabla C \cdot \nabla x_1 = 0 \tag{11}$$

Equations (8) and (11) form a set of mutually coupled nonlinear partial differential equations which are solved by standard finite element method.

With these equations one should associate adequate boundary conditions. At the inlet side we have

$$C = C_{given} \tag{12}$$

$$\frac{\partial x_1}{\partial n} = \frac{r_0}{D_1}(\gamma - x_1) \tag{13}$$

and at the proton membrane electrolyte side, where electrochemical reaction take place Neumann's boundary conditions have the form:

$$\frac{\partial C}{\partial n} = -\frac{vr_H x_1}{\Gamma(x,H)(\gamma_r - vx_1)} \tag{14}$$

$$\frac{\partial x_1}{\partial n} = -\frac{r_H}{D_1}x_1 \tag{15}$$

Thus all flux type boundary conditions depend not only on spatial coordinate but also on independent variable x_1.

3 An illustrative example

The schema of the two-dimensional cross section of the gas diffusion layer (GDL) cathode is shown on figure 1. The lower boundary at $y = 0$ represents the interface between the GDL and either the graphite plate or an open flow channel. The upper boundary, at $y = H$ corresponds to the plate catalyst layer separating the GDL and the PEM. Values of the constants and the geometry of the GDL cathode is given in [1] and will be not repeated here. The computational domain was divided into 382 finite elements of the third order and resulting system of linear equations had 1428 unknowns.
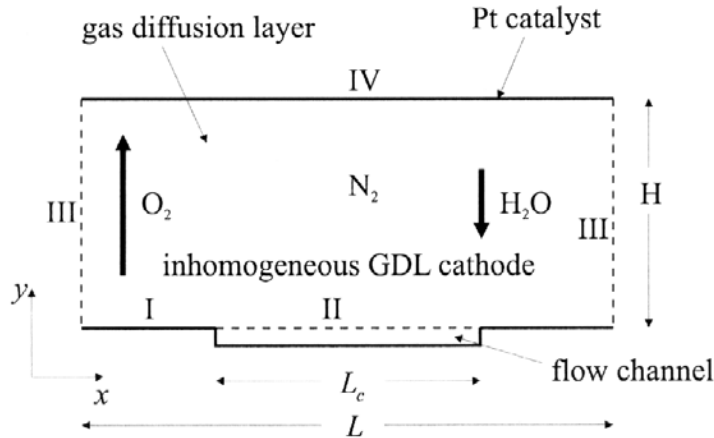

Fig.1. Gas diffusion layer with inhomogeneous porous material.

The flux of the convection Γ is shown on figure 2. We can see that the most influence of pollute particles clogging the electrode pores and decreasing the convection value is nearby flow channel and depends on average molar velocity

U. Closer to the catalyst layer the convection increases because of less pollution of the pores and at the $y = H$ the value of the convection is equal to the common value for GDL cathode where the inhomogeneous is not taken into considerations.

The flux of the flow of the vapour water is shown in fig. 3. We can see some disturbances of the flow nearby the channel, where convection inhomogeneous has the most influence to the flow.
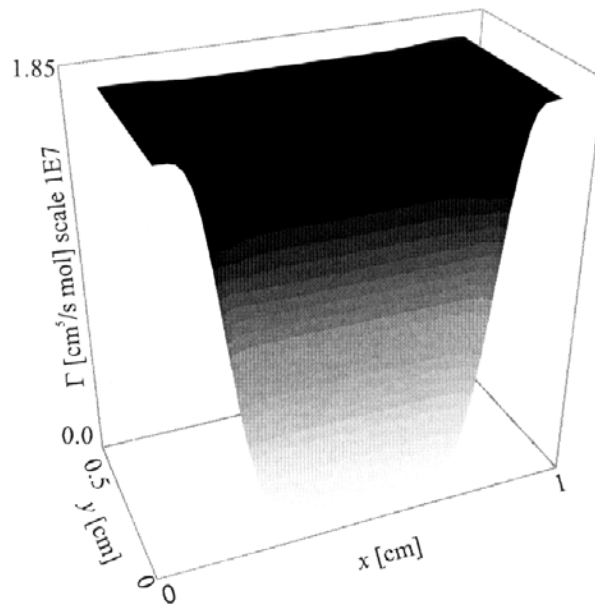
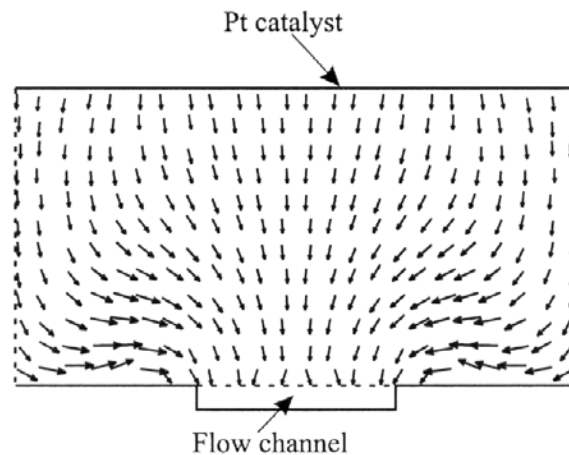

Fig.2. Convection flux Γ(x, y) in GDL anode.

Fig.3. Flux of the flow of the vapour water in GDL cathode.

At the fig. 4 and 5 we can see the influence of the inhomogeneous of the convection to the flux of the oxygen and the vapour water at the GDL cathode. The simulation of the pollution process was made by changing the K_1 coefficient

of the $\varGamma$ phenomenological relation (6). The coefficient may change at range from 0 to 1, where 0 means no pollution and 1 maximal pollution.

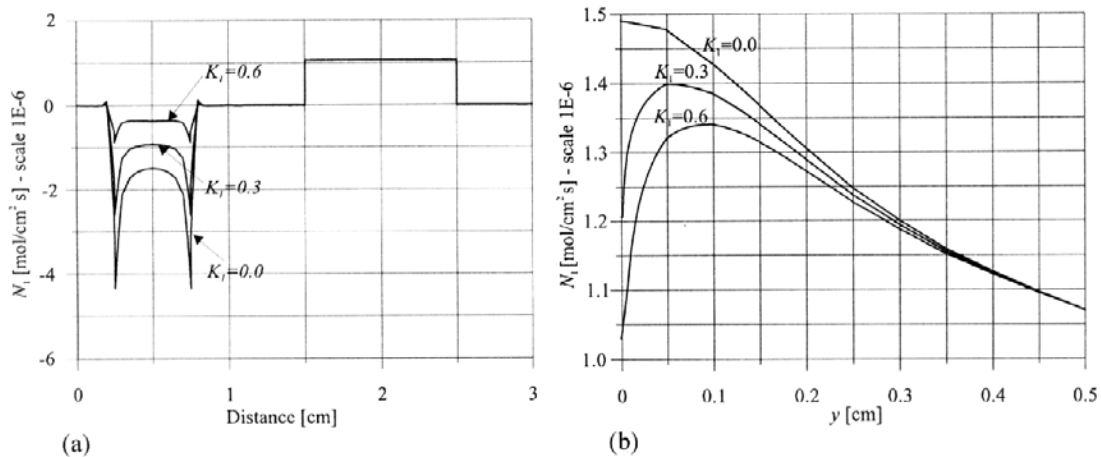(a)   (b)

Fig.3.Flux of the normal component of the oxygen on the boundary of the GDL cathode (a) and flux of the oxygen along $x = L/2$ line (b).

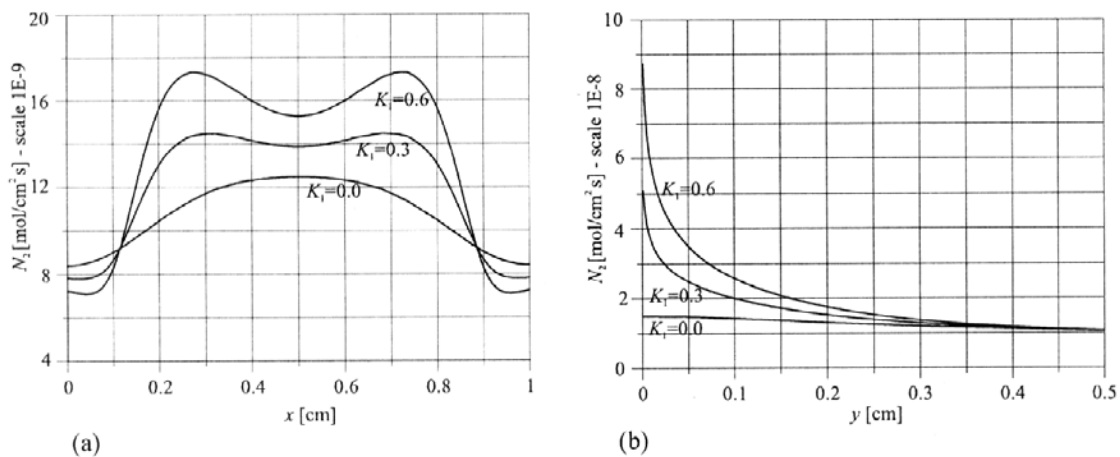(a)   (b)

Fig.4 Flux of the oxygen along $y = H/2$ line (a) and along $x = L/2$ line (b).

References

[1] K. Promislow, J. Stockie, Adiabatic relaxation of convective-diffusive gas transport in porous fuel cell electrode, *SIAM J. Appl. Math*, vol. 62, no 1, 2001, 180 – 205

[2] I-Ming Hsing, P. Futerko, Two-dimensional simulation of water transport in polymer electrolyte fuel cells, *Chemical Engineering Science*, vol. 55, 2000, 4209 – 4218

[3] J. S. Yi, T. V. Nguyen, Multicomponent transport in porous electrodes of proton exchange membrane fuel cells using the integrated gas distributors, *Journal of the Electrochemical Society*, vol. 146, no 1, 1999, 38 – 45.

[4] D. Singh, D.M. Lu, N. Djilali, A two-dimensional analysis of mass transport in proton exchange membrane fuel cells, J. Engrg. Sci. 37, 1999, 431–452

[5] R. B. Bird, W. E. Steward, E. N. Lightfood, *Transport Phenomena*, John Wiley & Sons, New York, 1960

[6] E. Kurgan, Fuel cells – their essence and futures, *Proc. of Seminar on Electrical Engineering BSE'2002*, vol. 14, Istebna, 2002