

DISTRIBUTION OF THE CURRENT DENSITY IN ELECTROLYTE OF THE PEM FUEL CELL

Eugeniusz Kurgan, Pawel Schmidt

AGH University of Science and Technology, Department of Electrical Engineering,
al. Mickiewicza 30, 30-059 Krakow, Poland,
e-mail: kurgan@agh.edu.pl, pschmidt@agh.edu.pl

Summary In this paper water management in proton exchange membrane (PEM) fuel cell is considered. First mass conservation law for water is applied. Next proton transport is described by the Nernst-Planck equation and liquid water convection velocity is eliminated by the Schlögl equation. Electro-osmotic drag coefficient is related to hydrogen index and experimentally determined swelling coefficient. Three partial differential equations for molar water concentration C_w , electric potential ϕ and water pressure P_w are formulated. Current density vector \mathbf{i} is derived from proton flux expression. These equations together with adequate boundary conditions were solved using finite element method. The distribution of electric potential and current density in function of geometrical parameters is investigated. At the end some illustrative example is given.

1. INTRODUCTION

One of the ways to understand a operation of fuel cells is to treat 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. Thus, since a fuel cell does not store energy internally but it is supplied externally, a fuel cell will not run down like a battery. Fuel cells directly convert the gaseous fuel into electricity whereas a battery has to be recharged from an external source. The fuels used by a fuel cell to generate electricity are hydrogen and oxygen [3]. Hydrogen is rarely found in its pure form. Most fuel cells employ a device called a reformer to extract hydrogen from hydrogen rich other fuels, as earth gas, oil and etc. The by-products of such reactions are carbon dioxide, less than half the amount generated by traditional electricity generation methods, and fast no of nitrous oxide. The type and the reforming reactions are hardly dependent on the type of fuel cell [4]. This article describes the electrochemical reactions and energetic consideration in a typical proton exchange membrane (PEM) fuel cell

2. PRELIMINARY CONSIDERATIONS

In proton exchange membrane fuel cell water and proton transport are driven by potential, diffusion and pressure gradients. Water is mainly produced at membrane-cathode interface in electrochemical reaction, but also it can be supplied from anode side, because of humidify of anodic inlet gases. The water molecules are dragging from anode to cathode by migrating protons which are on the other side moved back by diffusion process of water from cathode to anode. When current density electro-osmotic drag dominates over water diffusion process then dehydration on the anode side of the membrane may occurred.

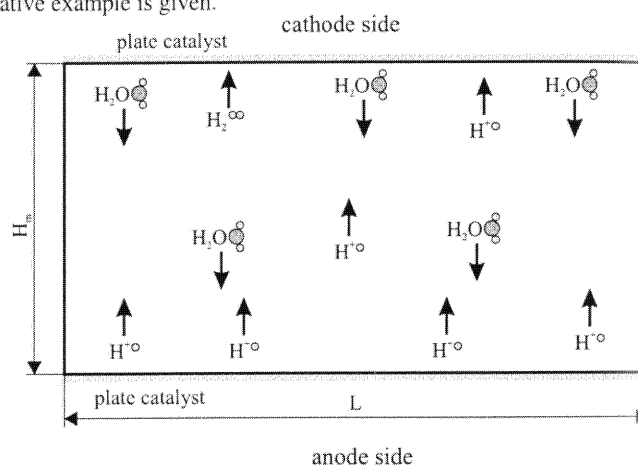


Fig.1. Computational domain together with geometrical dimensions.

In order to avoid membrane dehydration, adequate water management schemes that rely on the humidification of the anodic and cathodic gases are employed. Such procedure requires adequate balancing osmotic drag and diffusion process in order to avoid excessive water condensation of the gas diffusion layers that can flood the pores and prevent diffusing gases to the reaction sites. Also membrane from the anode side should be adequate hydrated.

In this article the empirical model proposed in [5] relating drag coefficient with molar water condensation is employed. Extending earlier modeling studies this paper presents two-dimensional isothermal model of the partially-hydrated membrane. The main goal of this publication is focused on calculation electric potential and current density distribution. In order to attain this goal first liquid water and proton molar concentrations are to be calculated.

3. MAIN EQUATIONS

Molar flux of liquid water in polymer membrane is governed by the following three processes: electro-osmotic drag, diffusion process of water molecules driven by concentration gradients and convection driven by pressure gradient:

$$\mathbf{N}_w = \frac{n_d}{F} \mathbf{i} - D_w \nabla C_w - C_w \frac{k_h}{\mu_l} \varepsilon_w^m \nabla p_w \quad (1)$$

where n_d is electro-osmotic drag coefficient, F is Faraday's constant, \mathbf{i} is current density vector, D_w is water diffusion coefficient, C_w is molar concentration of water, k_h is water permeability of membrane, μ_l is viscosity of water, ε_w^m is the volume fraction of water in membrane and p_w is the pressure of liquid water.

The electro-osmotic drag coefficient n_d is given by [5]:

$$n_d = \frac{2.5}{22} \lambda \quad (2)$$

where λ is the hydration index which is relating to C_w through following empirical formula:

$$C_w = \frac{e\lambda}{f\lambda + 1} \quad (3)$$

Here, f is empirical swelling coefficient for the membrane and e is expressed as:

$$e = \frac{\rho_m^{dry}}{E_m} \quad (4)$$

where ρ_m^{dry} is a density of the dry membrane and E_m is the equivalent membrane weight. Using above dependencies we can express n_d coefficient as:

$$n_d = \frac{2.5}{22} \frac{C_w}{(e - C_w f)} \quad (5)$$

Because water is not produced in the bulk of the electrolyte, divergence of the water flux has to be zero:

$$\nabla \cdot \mathbf{N}_w = 0 \quad (6)$$

Introducing (1) into the above relation we get:

$$\nabla \cdot \left(\frac{n_d}{F} \mathbf{i} - D_w \nabla C_w - \frac{k_h}{\mu_l} \varepsilon_w^m C_w \nabla p_w \right) = 0 \quad (7)$$

Because $\nabla \cdot \mathbf{i} = 0$ and $\nabla^2 p_w = 0$ we have [7]:

$$\frac{1}{F} \nabla n_d \cdot \mathbf{i} - D_w \nabla^2 C_w - \frac{k_h}{\mu_l} \varepsilon_w^m \nabla C_w \cdot \nabla p_w = 0 \quad (8)$$

Introducing the electro-osmotic drag coefficient n_d into above formula we get first partial differential equation describing the problem:

$$D_w \nabla^2 C_w + \frac{k_h}{\mu_l} \varepsilon_w^m \nabla C_w \cdot \nabla p_w - \frac{2.5}{22} \frac{e}{F} \frac{1}{C_p^2} \nabla C_w \cdot \mathbf{i} = 0 \quad (9)$$

Now we have to express current density vector \mathbf{i} in terms of C_w , p_w and ϕ . We start with general expression for \mathbf{i} :

$$\mathbf{i} = F \sum_{i=1}^n Z_i \mathbf{N}_i \quad (10)$$

where Z_i is a charge number and \mathbf{N}_i is an flux of the ionic species. Because in the PEM the only charged species are the protons, thus $n = 1$ and:

$$\mathbf{i} = F \mathbf{N}_p \quad (11)$$

The proton flux \mathbf{N}_p is described by the Nerst-Planck equation:

$$\mathbf{N}_p = -Z_p \frac{F}{RT} D_p C_p \nabla \phi - D_p \nabla C_p + C_p \mathbf{U}_w \quad (12)$$

The velocity of the liquid water \mathbf{U}_w is assumed to fulfill Schlögl equation:

$$\mathbf{U}_w = \varepsilon_w^m \left(\frac{k_\phi}{\mu_l} Z_f C_f F \nabla \phi - \frac{k_h}{\mu_l} \nabla p_w \right) \quad (13)$$

where Z_f is the charge number of the fixed charges and C_f is the fixed-charge concentration. Introducing Schlögl equation into Nerst-Planck equation we get:

$$\mathbf{N}_p = \left(-Z_p \frac{F}{RT} D_p C_p + \frac{k_\phi}{\mu_l} \varepsilon_w^m F Z_f C_f C_p \right) \nabla \phi - D_p \nabla C_p - \frac{k_h}{\mu_l} \varepsilon_w^m C_p \nabla p_w \quad (14)$$

Because of electroneutrality of PEM [8]:

$$Z_f C_f + \sum_{i=1}^n Z_i C_i = 0 \quad (15)$$

we get:

$$Z_f C_f = -Z_p C_p = -C_p \quad (16)$$

$$\mathbf{N}_p = - \left(\frac{F}{RT} D_p C_p + \frac{k_\phi}{\mu_l} \varepsilon_w^m F C_p^2 \right) \nabla \phi - D_p \nabla C_p - \frac{k_h}{\mu_l} \varepsilon_w^m C_p \nabla p_w \quad (17)$$

Current density given by (11) can be written in extended form as:

$$\mathbf{i} = - \left(\frac{D_p}{RT} + \frac{k_\phi \varepsilon_w^m}{\mu_l} C_p \right) F^2 C_p \nabla \phi - F D_p \nabla C_p - F \frac{k_h}{\mu_l} \varepsilon_w^m C_p \nabla p_w \quad (18)$$

Let us define proton conductivity in polymer membrane as:

$$\kappa = \left(\frac{D_p}{RT} + \frac{k_\phi \varepsilon_w^m}{\mu_l} C_p \right) F^2 C_p \quad (19)$$

so the equation (18) can be expressed as:

$$\mathbf{i} = -\kappa \nabla \phi - F D_p \nabla C_p - F \frac{k_h}{\mu_l} \varepsilon_w^m C_p \nabla p_w \quad (20)$$

Introducing κ into (17) gives:

$$\mathbf{N}_p = -\frac{\kappa}{F}\nabla\phi - D_p\nabla C_p - \frac{k_h}{\mu_i}\varepsilon_w^m C_p \nabla p_w \quad (21)$$

Now proton concentration C_p should be related to water concentration C_w . Similarly to equation (3) for water concentration also proton concentration can be described by relation [1,5]:

$$C_p = \frac{e}{f\lambda + 1} \quad (22)$$

thus:

$$C_p = e - fC_w \quad (23)$$

Current density vector \mathbf{i} can be expressed now as [8]:

$$\mathbf{i} = -\kappa\nabla\phi + fFD_p\nabla C_w - F\frac{k_h\varepsilon_w^m}{\mu_i}C_p\nabla p_w \quad (24)$$

Because of molar conservation law $\nabla \cdot \mathbf{N}_p = 0$ we have:

$$\nabla \cdot \mathbf{N}_p = -\frac{\kappa}{F}\nabla^2\phi - D_p\nabla^2 C_p - \frac{k_h}{\mu_i}\varepsilon_w^m\nabla(C_p\nabla p_w) = 0 \quad (25)$$

After introducing C_p :

$$\nabla^2\phi - \frac{FfD_p}{\kappa}\nabla^2 C_w - \frac{k_h Ff\varepsilon_w^m}{\mu_i\kappa}\nabla C_w \cdot \nabla p_w = 0 \quad (26)$$

From (9) we have:

$$\nabla^2 C_w = -\frac{k_h}{\mu_i D_w}\varepsilon_w^m\nabla C_w \cdot \nabla p_w + \frac{2.5}{22}\frac{e}{F D_w C_p}\nabla C_w \cdot \mathbf{i} \quad (27)$$

Introducing the above formula into (26) we get the second final partial differential equation:

$$\nabla^2\phi + \frac{Ffk_h\varepsilon_w^m}{\mu_i\kappa}\left(\frac{D_p}{D_w}-1\right)\nabla C_w \cdot \nabla p_w - \frac{2.5}{22}\frac{fD_p e}{\kappa D_w C_p^2}\nabla C_w \cdot \mathbf{i} = 0 \quad (28)$$

Third partial differential equations is the assumption of linear distribution of liquid water pressure [1]:

$$\nabla^2 p_w = 0 \quad (29)$$

4. BOUNDARY CONDITIONS

Boundary conditions used in this numerical simulation have following values [1, 2, 6]:

- from anode side: $C_w = 3.75 \cdot 10^{-6}$ [mol/cm³], $\phi = 0$ [V], $p_w = 3$ [atm],

- from cathode side: $C_w = 9.5 \cdot 10^{-6}$ [mol/cm³], $\phi = -1.2(1.5(x-L/2)^2 + 0.6)$ [V], $p_w = 5$ [atm],

5. ILLUSTRATIVE EXAMPLE

Geometrical dimensions of the analyzed problem are given in fig. 1. Following physical parameters of membrane model are used [1,2]:

$F = 96485$ [C/mol], $k_h = 1.58E-14$ [cm²], $k_p = 7.18E-16$ [cm²], $e = 0.0018$ [mol/cm³], $f = 0.0126$, $\mu_i = 3.56E-3$,

$D_p = 4.5E-5$ [cm²/s], $D_w = 0.2 D_p$, $\varepsilon_w^m = 0.28$, $T = 353$ [K], $R = 8.31451$ [J/mol.K], $\kappa = 0.17$.

The set of equations (9),(28) and (29) together with (20) and the adequate boundary conditions were solved using two-dimensional finite element method. The computational domain was divided into 244 finite elements of the third order, what gives 960 nodes and 2880 degrees of freedom.

In the fig 2. the equipotential line distribution is presented. Uniformity of the lines at the cathode side results from the non-uniform distribution of the potential on the catalytic layer. This uniformity of the other side, is a consequence of the non-uniform distribution of the

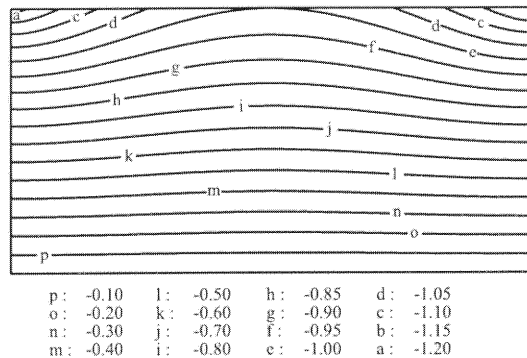


Fig.2. Equipotential lines distribution of the electric potential ϕ in the membrane of the PEM fuel cell.

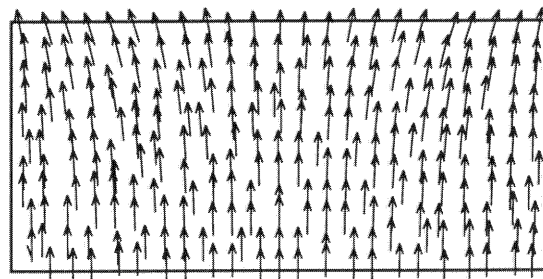


Fig.3. Current density vector \mathbf{i} represented in vector form.

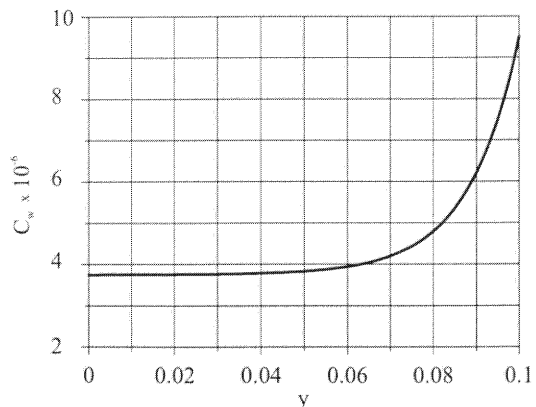


Fig.4. Distribution of molar concentration of water C_w along the line from $(L/2, 0)$ to $(L/2, H_m)$ given in [mol/cm².s].

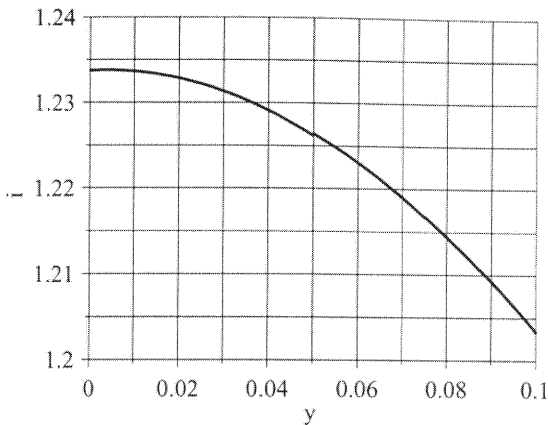


Fig. 5. Distribution of the magnitude of the current density vector i along the line from $(L/2, 0)$ to $(L/2, H_m)$ given in $[A/cm^2]$.

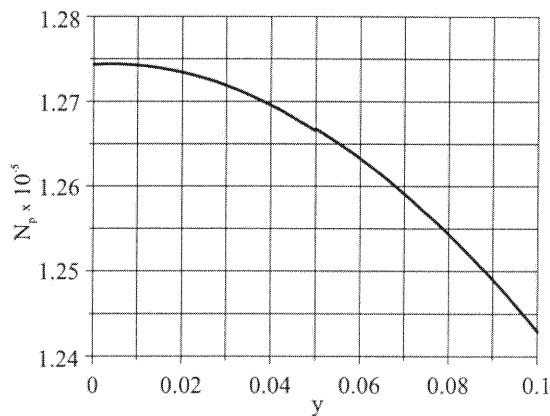


Fig. 6. Dependence between magnitude of the proton flux and the coordinate y from $(L/2, 0)$ to $(L/2, H_m)$ given in $[mol/cm^2.s]$.

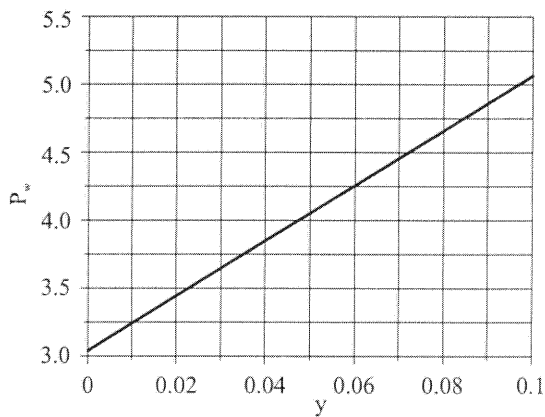


Fig. 7. Distribution of liquid water pressure P_w in atm along the line from $(L/2, 0)$ to $(L/2, H_m)$.

reacting species on the membrane-cathode surface. In the fig. 3 current density vector i in the vector form is presented. The direction of this current is consistent with flow of the protons flux N_p .

In the fig. 4. molar concentration of the liquid water across the membrane is plotted. The concentration has the greater value at the cathode side because of production of water during the electrochemical reaction on the cathode catalyst layer.

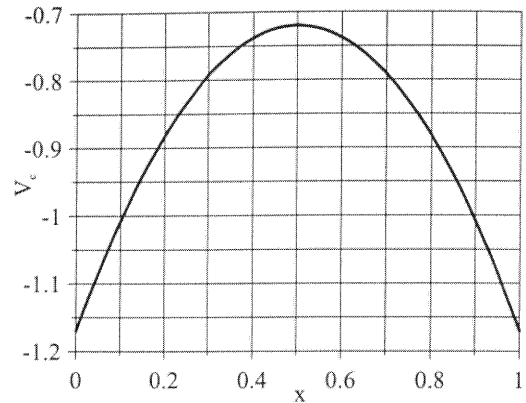


Fig. 8. Distribution of the potential on the catalytic layer at the cathode side given in $[V]$.

In the figs. 5 and 6 distribution of the magnitude of the current density vector i and proton flux N_p across the membrane is presented. The value of this current decreases with the y coordinate because protons are consumed at the anode side in the electrochemical reaction between protons, molecular oxygen and electrons which takes place on the catalytic layer.

In the fig 7 dependence between liquid water pressure and y coordination is shown. Because of assumption that pressure obeys the Laplace equation the dependence from spatial coordinate is linear. The assumed distribution of the electrical potential at the electrolyte-cathode boundary is shown in fig 8. This function is the result of numerical simulation of the distribution of the reactant gas components in the gas diffusion layer [6].

Acknowledgement

This work was supported by the AGH University of Science and Technology, under grant 11.11.120.183.

REFERENCES

- [1] J. Cao, N. Djilali, Computational simulation of water transport in PEM fuel cells using an improved membrane model, *10th Canadian Hydrogen Conference*, Quebec City, May 2000, pp. 447 – 456.
- [2] D. Bernardi, M.W. Verbrugge, Mathematical model of a gas diffusion electrode bonded to a polymer electrode, *Journal of the Electrochemical Society*, vol. 139, no 9, 1992, pp. 2477–2490.
- [3] D.Singh, D.M. Lu, N. Djilali, A two-dimensional analysis of mass transport in proton exchange membrane fuel cells, *International Journal of Engineering Science*, vol. 37, 1999, pp. 431 – 452.
- [4] S. Dutta, S. Shimpalee, J.W. Van Zee, Three-dimensional numerical simulation of straight channel PEM fuel cells, *Journal of Applied Electrochemistry*, vol. 30, 2000, pp. 115 – 146.
- [5] T.E. Springer, T.A. Zawodzinski, S. Gottesfeld, Polymer-electrolyte fuel cell model, *J. Electrochem. Soc.*, vol. 138, no. 8, 1991, pp 2334 – 2342
- [6] E. Kurgan, P. Schmidt, Time Dependence of Species Concentrations in Cathode of The PEM Fuel Cell, *The Second Polish-Slovenian Joint Seminar*

on Computational and Applied Electromagnetics, Kraków, 2003, 27 – 30.

- [7] J. Newmann, *Electrochemical Systems*, Prentice-Hall, Englewood Cliffs, N. J., 1973.
- [8] T. Berning, *Three-dimensional computational analysis of transport phenomena in a PEM fuel cell*, PhD Dissertation, RWTH Aachen, 1997.