Numerical Study of Effects of Gas Diffusion Layer Porosity Variation on Performance of PEM Fuel Cell

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Abstract—This paper investigates effects of variable gas diffusion layer (GDL) porosity on proton exchange membrane (PEM) fuel cell porosity. The half-cell model considers the cathode side of PEM fuel cell, extending from gas channel to membrane, is assumed and numerically solved. Eight continuous GDL porosity functions, are employed which four of them have equal mean value. The results show, higher GDL mean value porosity and uniformity of porosity distribution at equal mean value porosity leads to more oxygen diffusion into the GDL, therefore higher oxygen consumption in the catalyst layer, and increasing reaction rate at the catalyst layer, more current density is generated, higher loss of membrane phase potential which leads to better performance of fuel cell. The resulted polarization curves, for the GDL porosity models with equal mean value, imply that the distribution of the pore size is more important parameter than the total porosity. Effects of GDL length change are examined and it is shown that decreasing in GDL length at same surface overpotential value results in oxygen mass fraction and current density decrease and membrane phase over-potential increase; but there is an intermediate thickness of GDL, which leads to better fuel cell performance. Obtained results verified using former analytical and experimental data.

Keywords—PEM fuel cell; variable porosity; gas diffusion layer; Guassian function

I. INTRODUCTION

Portable devices have found numerous applications in recent years. To provide the required power for a portable device including Li-ion batteries and small fuel cells, different technologies are available [1,2]. Fuel cells offer the potential to replace batteries for such applications. PEM fuel cells are environmentally friendly power sources for both mobile and stationary application because of the attributes of high energy density at low operating temperature, zero emissions and minimal problems from component corrosion or electrolyte leakage. Nevertheless, two key issues limiting the widespread commercialization of fuel cell technology are better performance and lower cost. PEM fuel cell performance is limited by polarization. There are different kinds of polarization which is caused by kinetics of the electrochemical reactions, internal electronic and ionic resistance, internal currents and crossover reactants [3,6]. Optimum performance of the catalyst layer and electrode influenced by the properties of diffusion layer [7]. The surface area and porosity of gas diffusion layer (GDL) allow the reactants in the channel of the bipolar plate to diffuse along the active area (catalyst area) of the membrane. The GDL also handles the fuel cell moisture control. Bernardi [8] presented a mathematical model of the solid-polymer-electrolyte fuel cell that identifies operating conditions which result in a water balance. Vebrugge and Hil [9,10] developed a one dimensional model for the proton exchange membrane (MEA) based on the Nernst-Plank equation. Bernardi and Verbrugge [11,12] developed the necessary mathematical framework to simulate a fuel cell electrode bond to a membrane, later they developed a one dimensional, isothermal model for the cell.

The hydrophobicity of the diffusion layer may interact with the amount of water available for hydration at the membrane. The pores in the electrode full fill by liquid water which produces a dead zone and reduces the effective area, on the other hand, the porosity of gas diffusion layer can also change due to applied compression. It has been recognized that the performance of the fuel cell can be significantly influenced by porosity distribution [13-16]. H.K. Lee et al. [17] investigated the optimum porosity and thickness of gas diffusion layer and analyzed the variables related to electrode by simulation. The conditions leading to an optimized diffusion layer in which parameters were varied, are reported by L.R. Jordan et al. [18].

L. Giorgi et al. [19] studied the influence of the diffusion layer porosity on the effective catalyst activity for the cathodic oxygen reduction. R. Rohandel et al. [20] investigated the fuel cell performance by considering the effects of porosity variation distribution in GDL. The porosity variation in the GDL is calculated by considering the applied pressure and the amount of the water generated in the cell. Gurau et al. [21] developed a one dimensional half-cell model for the porosity of the GDL nonuniformity and analytical solution of the model is obtained. The presence of liquid water in GDL and catalyst layer is taken into account by means of effective porosity in which the gas diffuser in the model is represented by a series of parallel layers defined by different porosity and tortuosity coefficient. H.S Chu et al. [22] investigated the effects of nonuniform porosity across the GDL on performance of PEM fuel cell, based on half-cell model by employing four continuous functions of position.

In this study, fuel cell performance is investigated by solved numerically the half-cell model which proposed by Gurau et al.
II. MODEL DESCRIPTION AND ASSUMPTIONS

A. Assumptions

Fig. 1 shows the cathode electrode schematic of a PEM fuel cell [22]. The following assumptions are made to simplify the analysis: a) The model is one-dimensional b) The system is isothermal c) The air is fully saturated with water vapor, prior entering the fuel cell d) across the gas channel, gas diffuser and catalyst layer, diffusion is the only mode of transport e) The oxygen reduction reaction (ORR) is reversible and first order in oxygen f) oxygen is transported to the catalyst sites as a gaseous component

To take account the presence of liquid water, in this study, the porosity of GDL will be continuous function of position across the gas diffusion layer instead of uniform porosity or series parallel layer defined by different porosity-tortuosity coefficient. The porosity functions of GDL which considered in this investigation are described in Table 1 and shown in Fig. 2, where $\varepsilon_d$ is porosity function of the GDL.

B. Governing Equation of Oxygen Mass Fraction

The species are only transported across gas channel, gas diffuser layers and catalyst layer by diffusion. The transport equation for the oxygen mass fraction in the gas channel is:

$$\frac{d}{dx} \left( \rho D_{O_2} \frac{dY_g}{dx} \right) = 0 \quad 0 \leq x \leq L_x \quad (1)$$

![Physical model](image)

Fig. 1. Physical model

In this equation $\rho$ is the density of mixed gases, $D_{O_2}$ is the diffusion coefficient of oxygen, $Y_g$ is the oxygen mass fraction in the gas channel and $x$ is position. While in the gas diffusion layer the transport equation for oxygen mass function becomes:

$$\frac{d}{dx} \left( \rho D_{O_2}^{eff} \frac{dY_g}{dx} \right) = 0 \quad L_x \leq x \leq L_d \quad (2)$$

where $D_{O_2}^{eff}$ is effective diffusion coefficient in porous media and $Y_g$ is oxygen mass fraction in the GDL. The Bruggeman-type correction for the effective diffusion coefficient in porous media, can be applied through this derivation [23]:

$$D_{O_2}^{eff} = \varepsilon_d^{m} (x) D_{O_2} \quad (3)$$

where $\tau_d$ is tortuosity factor of GDL. Replacing Bruggeman-type correction, (2) becomes:

$$\frac{d}{dx} \left( \varepsilon_d^{m} (x) \rho D_{O_2} \frac{dY_g}{dx} \right) = 0 \quad L_x \leq x \leq L_d \quad (4)$$

Under assumption that the ORR is irreversible and first order in oxygen and that electro neutrality in any representative

![Porosity distribution function](image)

Fig. 2. Porosity distribution function of eight considered models

Table 1. GDL Porosity Function

<table>
<thead>
<tr>
<th>Model</th>
<th>Gas Diffusion Layer Porosity function</th>
<th>Mean value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\varepsilon_d(x) = 0.4$</td>
<td>0.4</td>
</tr>
<tr>
<td>2</td>
<td>$\varepsilon_d(x) = -1142.8571x + 0.7$</td>
<td>0.50004</td>
</tr>
<tr>
<td>3</td>
<td>$\varepsilon_d(x) = \exp((-7.5 \times 10^3)x^2 - (2.04 \times 10^2)x - 0.0357)$</td>
<td>0.5177</td>
</tr>
<tr>
<td>4</td>
<td>$\varepsilon_d(x) = \exp((-7.5 \times 10^3)x^2 - (5.05 \times 10^2)x - 0.0357)$</td>
<td>0.495</td>
</tr>
<tr>
<td>5</td>
<td>$\varepsilon_d(x) = 0.57$</td>
<td>0.57</td>
</tr>
<tr>
<td>6</td>
<td>$\varepsilon_d(x) = -742.8571x + 0.7$</td>
<td>0.57</td>
</tr>
<tr>
<td>7</td>
<td>$\varepsilon_d(x) = \left( \frac{1}{q \sqrt{\pi}} \right) \exp \left( \frac{(-4.6286 \times 10^2)x - 0.0811)^2}{2q^2} \right)$</td>
<td>0.57</td>
</tr>
<tr>
<td>8</td>
<td>$\varepsilon_d(x) = \exp((-9.9811)x^2 + (9.7252)x - 0.3567)$</td>
<td>0.57</td>
</tr>
</tbody>
</table>
Elementary volume, the cathode transfer current density can be expressed as:

$$ J = n_i F K Y_e \exp \left( (\alpha n_i F / R T) \eta \right) $$

(5)

where $F$ is Faraday constant, $K$ is the reaction rate constant, $\alpha$ is transfer coefficient and in this study is taken account 0.56, $\eta$ is the surface over potential, $R$ is universal gas constant, $n_i$ is number of electrons participating in reaction and $T$ is the absolute temperature. In the catalyst layer the oxygen is consumed and the transport equation becomes:

$$ \frac{d}{dx} \left( \varepsilon_i \rho D_{i Y_e} \frac{dY_e}{dx} - J \frac{1}{2n_i F M_{o_2}} \right) = 0 \quad L_d \leq x \leq L_c $$

(6)

where $\varepsilon_i$ and $\tau$ are the uniform porosity and tortuosity factor of catalyst layer, respectively, $Y_{o_2}$ is the oxygen mass fraction in the catalyst layer and $M_{o_2}$ is the molecular mass of oxygen.

The boundary conditions are:

- At the beginning of the gas channel:
  $$ Y_e = Y_0 \quad x = 0 $$
  (7)

- At the gas channel and gas diffuser interface:
  $$ Y_e = Y_d \quad x = L_d $$
  (8)

- Conservation of oxygen and oxygen flux at the gas diffuser and catalyst layer:
  $$ \varepsilon_i \frac{dY_e}{dx} = \varepsilon_i \frac{dY_e}{dx} \quad x = L_d $$
  (9)

- Conservation of potential and proton current at the gas diffuser and catalyst layer:
  $$ \frac{dY_e}{dx} = 0 \quad x = L_c $$
  (10)

- Conservation of potential and proton current at the gas diffuser and catalyst layer:
  $$ \frac{dY_e}{dx} = 0 \quad x = L_c $$
  (11)

- At the catalyst layer and membrane interface
  $$ dy / dx = 0 \quad x = L_c $$
  (12)

The density computed from the ideal gas law [23]:

$$ \rho = PM / RT $$

(13)

where $P$ is the pressure and $M$ is molecular mass. Gas mixture molecular is calculated from:

$$ M = \frac{1}{1 - \frac{Y_{o_2}}{M_{o_2}}} + \frac{Y_{o_2}}{M_{o_2}} \left[ 1 - Y_w - \frac{Y_{o_2}}{M_{o_2}} \right] $$

(14)

where $Y_{o_2}$ is the water vapor mass fraction, and the subscripts $o_2$, $W$, $N_2$ mean oxygen, water vapor and nitrogen respectively. The mass fraction of the saturated water vapor is:

$$ Y_w = \left( \frac{P_{sat}^w}{P} \right) \times \left( \frac{M_w}{M} \right) $$

(15)

where $P_{sat}^w$ is the water saturation pressure and calculated from the following expression [25]:

$$ \log_{10} \left( \frac{P_{sat}^w}{P} \right) = \frac{-2.1794 + 0.02953(T - 273.15)}{10^5 (T - 273.15)^3} + 1.4454 \times 10^{-7} (T - 273.15)^4 $$

(16)

Replacing $Y_w$ which is calculated by (15), (14) becomes:

$$ M_i = \left( 1 - \frac{P_{sat}^w}{P} - \frac{P_{sat}^o M_w}{PM_{N_2}} \right) \left( \frac{Y_{o_2}}{M_{o_2}} + \frac{1}{M_{N_2}} - \frac{Y_{o_2}}{M_{N_2}} \right) $$

(17)

In addition the diffusion coefficient is a function of temperature and pressure [24]:

$$ D_{k,m} (T) = (D_{k,m})_0 (T/T_i)^{1.5} (P_i/P_f) $$

(18)

C. Governing equation of membrane phase potential:

The average surface over potential across the catalyst layer as a set parameter, is used to decouple the systems of equation. In the catalyst layer, the equation becomes:

$$ \frac{d}{dx} \left( \varepsilon_i \sigma \frac{d\Phi_m}{dx} \right) = J \quad L_d \leq x \leq L_c $$

(19)

where $\varepsilon_i$ and $\tau_{iron}$ are the porosity and tortuosity of the ionmer in the catalyst layer, respectively and $\Phi_m$ is the membrane phase potential in the catalyst layer. In the membrane, the expression for the membrane phase potential is:

$$ \frac{d}{dx} \left( \sigma \frac{d\Phi_m}{dx} \right) = 0 \quad L_c \leq x \leq L_m $$

(20)

where $\sigma$ is the ionic conductivity of the membrane and $\Phi_m$ is the membrane phase potential in the membrane.

The following boundary conditions are apply:

- No proton leave the catalyst layer at the interface between the gas diffuser and the catalyst layer:
  $$ \frac{d\Phi_m}{dx} = 0 \quad x = L_d $$
  (21)

- Conservation of potential and proton current at the interface between the catalyst layer and the membrane:
  $$ \Phi = \Phi_m \quad x = L_c $$
  (22)

- Zero potential at the interface between the membrane and anode:
  $$ \Phi = 0 \quad x = L_m $$
  (23)

The membrane ionic conductivity, $\sigma$, can be obtained by the empirical expression [25]:

$$ \sigma = (0.5139 \lambda - 0.126) \exp \left( \left[ \frac{1/303 - 1/T_i}{10^5} \right] \right) $$

(25)

where $\lambda$ is the membrane water content at the interface. Under the assumption, the air is saturated before the cathode inlet, the water vapor activity will be everywhere equal to one. Under these conditions, the water produced in the cathode catalyst layer will be only in the liquid phase, and the membrane is unlikely to
dehydrate at the cathode side. In this case, it can be assumed that the water content in the ionomer is constant [21]. There are few empirical models available in the literature describing the water content in PEM fuel cells [23-25]. In present study, water content in catalyst layer is take account constant and, in membrane is estimated by linear profile [21]:

\[
\lambda = (\lambda_a - \lambda_c) / (L_m - L_c) \times (x - L_c) + \lambda_c, \quad L_c \leq x \leq L_m
\]

where \(\lambda_a\) is anode water content and \(\lambda_c\) is cathode water content. Governing equations of current density.

D. Governing equations of current density

In the membrane and catalyst layer, the current density is expressed by ohm's law for proton migration, the equations are become [21]:

\[
i_{cl} = \sigma_{cl} \frac{d\Phi}{dx}, \quad L_c \leq x \leq L_m
\]

\[
i_{m} = \sigma_{m} d\Phi / dx, \quad L_c \leq x \leq L_m
\]

where \(i\) is the current density, the subscript cl and m mean catalyst layer and membrane, respectively, and \(\sigma_{cl}\) is the membrane ionic conductivity at the cathode. Current density is easily can be calculated without employing boundary conditions, after obtaining the values of the membrane phase potential. When the surface overpotential is taken as the governing parameter of the system [21], the polarization curve can be subscribed parametrically by the relation between \(V(\eta)\) and \(I(\eta)\), where

\[
V(\eta) = V_o - \Delta \Phi(\eta) - \eta
\]

where \(V_o\) is the open circuit voltage.

E. Numerical Approach

In order to solve governing equations, a computational fluid dynamic (CFD) code was developed based on the finite difference numerical approach. The central difference scheme is applied.

III. RESULT AND DISCUSSION

This section is divided into two subsection: model validation and parametric study result. In the first subsection the computed data compared with experimental and analytical data, to prove CFD code. In the second subsection effects of five different models of the porosity of the GDL with different mean value, four different models of the porosity of the GDL in which the mean value are same and at last effect of electrode thickness, on the PEM fuel cell performance is investigated.

The base case conditions are same as those uses by Gurau et al. [21]. The reader is referred to their table 1 for the details.

A. Model Validation:

It is essential to compare the computed data with experimental and analytical data, to prove the validation of the CFD code. Because we were unable to perform this experiment, we can compare this study with the experimental condition reported by H. K. LEE et al. [17] and analytical data reported by Gurau et al. [21].

B. Parametric Study Results

1) Effects of variable porosities with different mean value in terms of physical parameters

a) effects on oxygen mass fraction

In this section, oxygen mass fraction profile along the gas channel and GDL with variable porosity and catalyst layer for different values of surface over-potential is investigated. Fig. 3 depicts the computational results. At the same surface over-potential, higher average porosity of GDL leads to smaller oxygen mass fraction in the gas channel, because of larger porosity of the GDL allows higher oxygen consumption in the catalyst layer. On the other hand for the case of low porosity, most of oxygen appears in gas channel but only little amount of oxygen can transport through the GDL, as the porosity increases, more oxygen enters the GDL and mass fraction of oxygen decreases along the gas channel and increases along the GDL. In this study, mass fraction of oxygen changes continuously with position based on porosity distribution across the GDL. For example, for Gaussian function with .57 mean value, more oxygen transport to GDL rather than other function and this result to smaller oxygen mass fraction in gas channel and at the beginning of GDL, where local porosity is smaller than average porosity, oxygen mass fraction decreases. Across the GDL, as porosity increased, oxygen mass fraction is increasing too. In other word, increasing porosity of GDL will enhance diffusion of oxygen into the GDL and increasing reaction rate at the catalyst layer. Fig. 3 also shows that at the same porosity of the GDL, increasing higher surface over-potential causes lower oxygen mass fraction in gas channel and GDL diffusion layer. This is due to larger surface over-potential corresponds to more active electrochemical reactions which lead to increase in oxygen consumption in gas channel and GDL. Because the catalyst layer is very thin and the electrochemical reaction within the layer prevails, the variation in the oxygen mass fraction along the catalyst layer is not all significant for all porosity function and all over-potential value.

b) effects on current density

GDL variable porosities with different mean value have effect on current density, which can be verified in Fig. 4. As Fig. 4 depicted, current density climbs up in catalyst layer and reaches to its limitation value at membrane, which increases with \(\eta\) because higher surface over potential results in more active electrochemical reaction and consequently more current density is generated. Higher porosity value in GDL results in higher current density, because increasing porosity value leads to more oxygen consumption and eventually higher current density is generated.

a) effects on membrane phase potential

The profile of membrane phase potential in the membrane and catalyst layer at different surface over potential are shown in Fig. 5. As shown in the Fig. 5, the membrane phase potential is lower for higher porosity value in GDL. The differences between membrane phase potentials increase due to surface over-potential increasing, which result in more active electrochemical reaction and consequently more oxygen consumption, thus larger current density is generated and this is result in higher loss of membrane phase potential.
In this study, the Gaussian function has lower membrane phase potential because of higher porosity value which leads to higher loss of membrane phase potential and better performance of PEM fuel cell.

These results are in agreement with the results reported by Guraue et.al [21] and H. S. Chu et al. [22]. This is implies the numerical method and CFD code is valid.

2) Effects of variable porosities with equal mean value in terms of physical parameters

Four different porosity function of GDL with equal mean value is investigated in this section.

**a) Effects on oxygen mass fraction**

Oxygen mass fraction profile across the gas channel, GDL with variable porosity and catalyst layer is shown in Fig. 6. As shown in Fig. 6, at same surface overpotential, oxygen mass fraction of exponential and Gaussian functions are higher than two other functions and porosity constant has the smallest oxygen mass fraction at the gas channel and GDL. According to these results, the distribution of the pore size is more important parameter than the total porosity since the different modes of gas and water transport regulated by the specific volumes of small and large pores. For the same reason stated before, increasing surface overpotential causes lower oxygen mass fraction in gas channel and gas diffusion layer.
b) Effects on current density

Effects of variable porosities with equal mean value on current density is shown in Fig. 7. As depicted in Fig. 7, for the same surface overpotential, the current density is higher for constant function and decreases due to increasing in variability of pore-size distribution, for example the Gaussian function has the lowest value. This is due to the fact that more uniformity in porosity distribution leads to larger oxygen transported to catalyst layer and therefore more oxygen consumes in catalyst layer and thus larger current density is generated. It can be seen in Fig. 7, current density generating increase due to increasing in surface over-potential value. This is because of more active electrochemical reaction.

a) Effects on membrane phase potential

In this section, membrane phase potential profile across the catalyst layer and the membrane is investigated. Fig. 8, depicts computational results. The membrane phase potential is lower when the porosity distribution is more uniform, which leads to larger current density, and thus higher loss of membrane phase potential. This study shows for variable porosity in GDL with equal mean value, more uniform porosity distribution leads to better PEM fuel cell performance, but results should compare to experimental data to find better porosity function approximation.

c) Effects on polarization curve

The polarization curve for these models, are shown in Fig. 9. The polarization curve of four models are approximately overlap at first and second region. Differences between curves increase due to increasing current density. This implies that the influence of GDL porosity is negligible at low or medium current density, while it becomes significant when current density is close to limiting value. This finding implies that limitation current density increase due to increasing uniformity of porosity distribution, because of transporting more oxygen across the gas channel and GDL to catalyst layer, therefore voltage drop corresponds to concentration polarization occurs at higher current density.

3) Effects of GDL length change with variable porosity in terms of physical parameters

A comparison of physical parameters of the electrodes with different thickness and the same catalyst layer in the electrode is investigated. Since the catalyst layer is the same, the performance difference is because of different thickness of GDL. The thickness of GDL is vary as 375, 350,322 (µm). This study is performed for Gaussian function porosity distribution, because, according to previous section results, it is shows more accurate approximation. As shown in Fig. 10, oxygen mass fraction decrease due to decreasing in GDL length at same η value. Current density decrease and membrane phase over-potential increase due to decreasing in GDL length at same surface over-potential value, as depicted in Fig. 11 and Fig. 12. The thickness of the diffusion layer has competing tendencies where, by the improvement in one property, another property will worsen. A thin layer improves the gas supply and facilitates the removal product of water, but it has high electronic resistance and does not give a nonpermeable support for coating with the catalyst layer during electrode fabrication. Therefore, permeation of the catalyst layer into the diffusion layer makes poor ionic contact with the Nafion membrane. On the other hand, a thick layer reduces the accessibility of gas due to the
lengthened path in the layer and has poor gas diffusivity. Hence, an intermediate thickness enhances the electrode performance best.

The results which are validated by comparing with polarization curve for PEM fuel cell with GDL total porosity 0.57 and variable pore distribution reported by H. K. Lee et al. [17] and the data reported by Gurau et al. [21].

In this study, the influence of variable porosity of GDL on PEM fuel cell is numerically investigated. Water content of GDL is taken into account by considering eight porosity continuous functions. Four functions have equal mean value. In summary, the following conclusions have been drawn:

- Higher average porosity of GDL leads to more oxygen diffusion into the GDL, therefore higher oxygen consumption in the catalyst layer, and thus increasing reaction rate at the catalyst layer.

IV. CONCLUSION
Decreasing in uniformity of porosity distribution leads to over-potential value, because of thin catalyst layer. The variation in the oxygen mass fraction along the catalyst layer and reaches to its limitation value at membrane, which increases with \( \eta \).

Higher average porosity of GDL leads to generating higher current density and higher loss of membrane phase potential, and thus, better PEM fuel cell performance which also corresponds to higher surface over-potential.

The distribution of the pore size is more important parameter than the total porosity since the different modes of gas and water transport regulated by the specific volumes of small and large pores.

Uniformity in porosity distribution leads to larger oxygen transported to catalyst layer and therefore more oxygen consumes in catalyst layer and thus larger current density is generated. It is leads to lower membrane phase potential.

Decreasing in uniformity of porosity distribution leads to better approximation of fuel cell performance. This study shows that, for GDL porosity, Gaussian function has the maximum potential to display fuel cell performance compared with experimental work.

Oxygen mass fraction decrease due to decreasing in GDL length at same \( \eta \) value. Current density decrease and membrane phase over-potential increase due to decreasing in GDL length at same surface over-potential value, but there is an intermediate thickness of GDL, which result in better fuel cell performance.

V. REFERENCES


