Using Comsol to Model the Cathode of a PEM Fuel Cell

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ABSTRACT

The cathode of a PEM fuel cell has been modeled using Darcy's Law and the Maxwell Stefan equation as the basic governing equations. The cathode was considered to be a porous diffusion layer. The temperature was 80°C and the pressure was approximately atmospheric pressure, with a slight increase of pressure at the oxygen inlet to the cathode to create flow through the cathode. Velocity, pressure, and the mass fractions of oxygen and water were the variables studied within this system. To compare the oxygen content at the cathode's interface with the polymer electrolyte membrane, a parametric study was done of the mass fraction of oxygen when both air and pure oxygen were used as the feed to the cathode.

Introduction

Since the U.S. is running out of domestic oil, a new fuel or energy policy must replace dependence on foreign oil. In addition, ever increasing carbon dioxide emissions from fossil fuels have been acknowledged as enhancing the greenhouse effect and causing global climate change. Part of a solution to this problem is using alternative energy to run our vehicles and supply electricity. Recently, hydrogen fuel cells have been seen as the solution to these problems. Four of President Bush's State of the Union Addresses have mentioned hydrogen automobiles. In one speech, he stated explicitly, "… let us promote hydrogen fuel cells as a way to advance into the 21st century" [1].

Of the various types of fuel cells, proton exchange membrane (PEM) fuel cells, also known as polymer electrolyte fuel cells, are one of the more practical choices. The PEM fuel cell is compact, which means that it could be used to run anything from a vehicle to a cell phone, and it operates well at ambient temperatures and pressures [2].

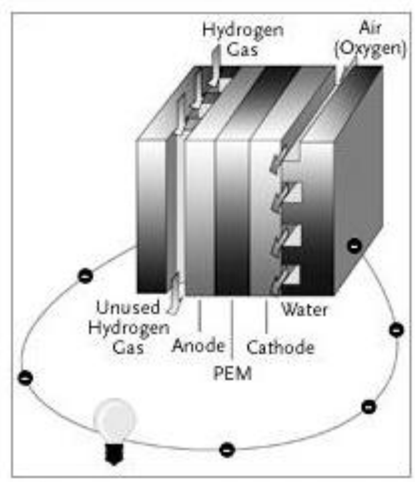


Figure 1

Figure 1 [3] shows the basic components of a PEM fuel cell system. This image depicts the hydrogen gas and air channels as being perpendicular, but the direction and shape of the channels vary from design to design. Figure 2 [11] shows a different channel arrangement and depicts a close up section of a cathode, with the basic parts labeled.

Mathematical modeling is an important way to test theories on what physical and chemical laws govern species' movements and interactions and what effects modifications to a system would have.

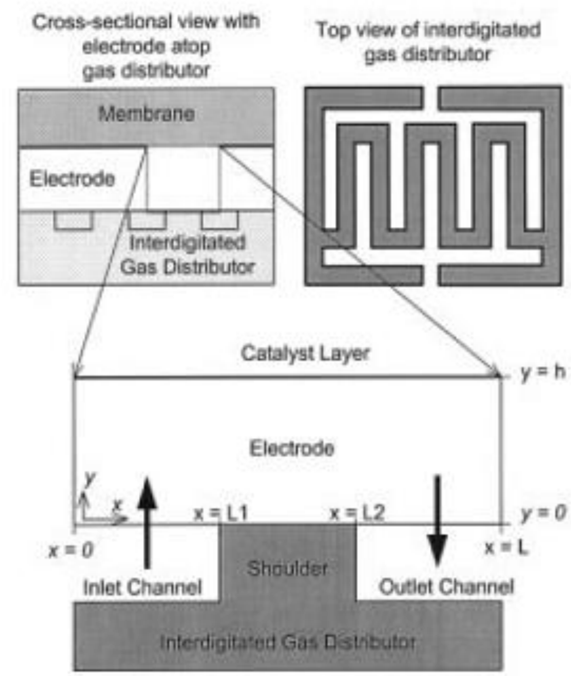


Figure 2

Several simple, one-dimensional models of fuel cells were produced in the early 1990s by Bernardi [5-7], Springer *et al.*, [8], and Nguyen and White [9]. These models greatly simplified complex systems. Next, psuedo-two dimensional models were developed by Fuller and Newman [10], Yi and Nguyen [11], and Thirumalai and White [12]. Fuller considered both the distance from the cathode and the distance from the entrance in various graphs but did not produce a comprehensive two dimensional image relating both of the coordinate directions. Yi and Newman discussed the y direction, and Thirumalai divides the flow field into elements, but neither incorporated two dimensions into their modeling equations.

Two-dimensional models did appear in the works of Guara *et al.* [13], Yi and Nguyen [14], and Um *et al.* [15]. Recently, efforts to determine equations that deal in three dimensions have been produced by Dutta *et al.* [16,17] and by Meng and Wang [18].

Both electrodes consist of platinum, but whereas platinum very effectively splits hydrogen molecules, it is not as effective at splitting the stronger oxygen molecules. This causes a significant loss of efficiency [2]. Therefore, particular attention has been paid to accurately analyzing the equations that govern the cathode and to improving the materiality of the cathode. Since mathematical modeling can indicate the effects of changes made to the cathode before extensive material and labor have been spent on the problem, modeling the cathode is particularly worthwhile.

Early models which focused on modeling the cathode, with special attention to transport properties, include works by Bernardi [7] and Springer [19]. A more detailed model, which concentrated on modeling the active catalyst layer, was produced by Broka and Ekdunge [20]. This paper will compile and utilize the more complex, two-dimensional equations which have been developed to model a PEM fuel cell cathode. Figure 3 depicts the outline of the cathode as it will be modeled in this paper. Each component can be identified with a component from the section shown in Figure 2 [11].

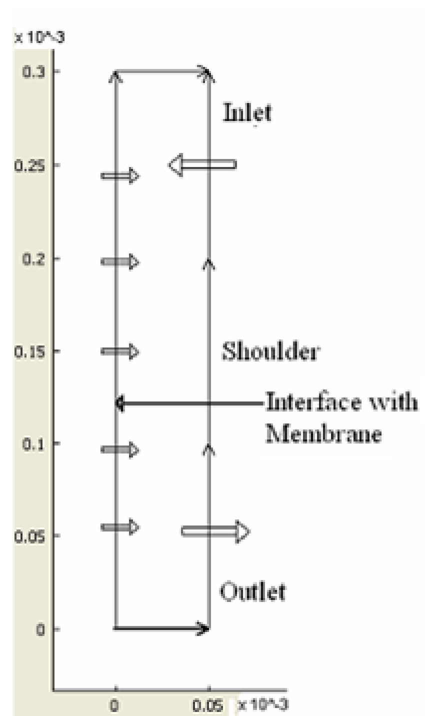


Figure 3

Governing Equations

According to the works of Yi and Nguyen [11] and Dutta *et al* [16-17], there are two basic governing equations that must be considered. The first equation combines the conservation of mass and momentum balance for ideal gases [11]. This equation, equation 1, is a form of Darcy's Law.

$$\nabla \cdot \left(-\frac{\kappa M}{\eta R T} p \nabla p \right) = 0 \qquad (1)$$

where κ is the permeability of the cathode, η is the dynamic viscosity, M is the average molar mass of the gas mixture (defined below), R is the ideal gas constant, T is the temperature, and p is the pressure.

The second type of governing equation deals with mass transport. Three species are present in the cathode: oxygen, O; water, w; and nitrogen, N. However, we do not need to consider nitrogen independently since it can be considered as a function of the mass fractions of oxygen and water, as given by Yi and Nguyen [11].

$$\omega_N = 1 - \omega_O - \omega_w \qquad (2)$$

Thus

$$M = \frac{1}{\frac{\omega_O}{M_O} + \frac{\omega_w}{M_w} + \frac{1 - \omega_O - \omega_w}{M_N}} \qquad (3)$$

where ω_i is the mass fraction of species *i* and M_i is the molar mass of species *i*.

The most appropriate equation for modeling mass balance within a cathode is given by the Maxwell-Stefan equation:

[illegible] (4)

where *t* is time, $\tilde{D}_{ij}$ represents the *ij* component of the Fick diffusivity matrix, so for example, D_{Ow} is the diffusion coefficient of water and oxygen, ρ is density, T is the temperature field, and R_i the reaction rate of species *i*. For the cathodic reaction, we have i = O and w.

From Yi and Nguyen [11], who stated that it was valid to assume ideal gases, the density can be found by the expression:

$$\rho = \frac{pM}{RT} \qquad (5)$$

The boundary conditions, based upon the information given by Yi and Nguyen [11] and Dutta [16] are given in Table 1.

Table 1

Boundary name	**Darcy's Law Boundary Condition**	**Maxwell-Stefan Boundary Condition**
Inlet	Pressure: p_{in}	Mass fraction: $\omega_{O,in}$, $\omega_{w,in}$
Outlet	Pressure: p_{out}	Convective Flux: $\frac{\partial \omega_O}{\partial x}=0, \frac{\partial \omega_w}{\partial x}=0$
Shoulder	Insulation	Insulation
Horizontal Boundaries	Insulation	Insulation
Boundary with Membrane	Inflow/Outflow: equation (8)	Flux: equations (6), (7)

[illegible] (6)

[illegible] (7)

[illegible] (8)

where α is the net water transport coefficient in the membrane, ε is the porosity of the electrode, k is the transfer coefficient of the oxygen reduction reaction, F is the Faraday constant, φ is the overpotential, and $a = I_0 / c_{0,ref}$ where I_0 is the exchange current density and $c_{0,ref}$ is the oxygen reference concentration for the oxygen reaction, and D_i^e is the effective molar diffusion coefficient of species i in the gas stream and $D_i^e = D_i \varepsilon$ where D_i is the diffusion coefficient in a nonporous system.

Solution

Table 2 gives the parameters that were used to model the cathode of a PEM fuel cell. Unless otherwise stated, the parameters given in Table 2 are from the work of Yi and Nguyen [11]. The combination diffusivities, D_{ij}, make up the diffusivity matrix that is used in the Maxwell-Stefan equation (eq. 4).

Several important variables can be identified through this ComSol model of a PEM fuel cell cathode. The velocity flow within the cathode is easily determined, giving both its maximum and minimum magnitudes and the flow path of species within the cathode. Figures 4 through 7 show the velocity of substances throughout the cathode. Figure 4 depicts velocity at the leftmost side of the cathode, when x=0m. Figure 5 shows velocity at the rightmost side of the cathode, when x=0.0005m. Figure 6 shows velocity profiles at five different x-values. The location of these profiles and the velocity profile can be seen in Figure 7. Determination of which x value belongs to which velocity profile can be made based upon Figures 4 and 5.

Table 2

Parameter	Value
T, temperature	80°C = 353.15K
κ, permeability	$1.0*10^{-8}$ N/atm = $9.9*10^{-14}$ m^2
ε, porosity	0.3
η , dynamic viscosity	$2.1*10^{-5}$ kg/m/s
D_O, diffusivity of oxygen	0.1775 cm^2/s = 1.775 * 10^{-5} m^2/s
D_w, diffusivity of water	0.256 cm^2/s = 2.56 * 10^{-5} m^2/s
a, current expression constant	0.0001 A/cm-mol O_2 = 0.01 A/m-mol O_2
k, transfer coefficient of oxygen reduction reaction	.5
φ, overpotential	0.3 V
α, net water transport coefficient of the membrane	0.1
$D_{O,w}$, diffusivity of oxygen and water [21]	.282 cm^2/s = 2.82 * 10^{-5} m^2/s
$D_{O,N2}$, diffusivity of oxygen and water [21]	.230 cm^2/s = 2.30 * 10^{-5} m^2/s
$D_{w,N2}$, diffusivity of water and nitrogen [21]	.293 cm^2/s = 2.93 * 10^{-5} m^2/s
$\omega_{O,in}$	.21
$\omega_{w,in}$	0.0
p_{in}	1.03 atm = $1.043*10^5$ Pa
p_{out}	1.00 atm = $1.013*10^5$ Pa

Figure 4

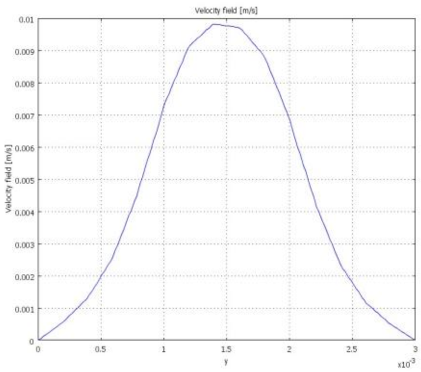


Figure 5

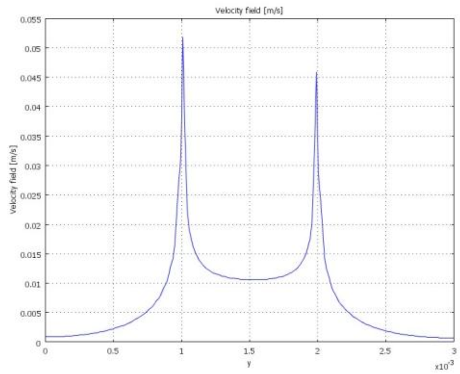
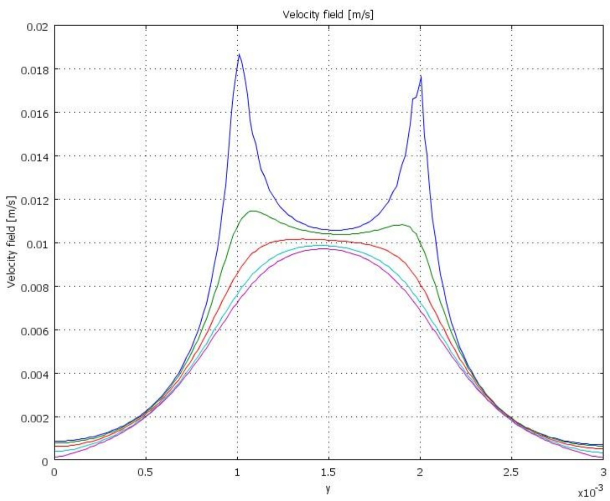


Figure 6



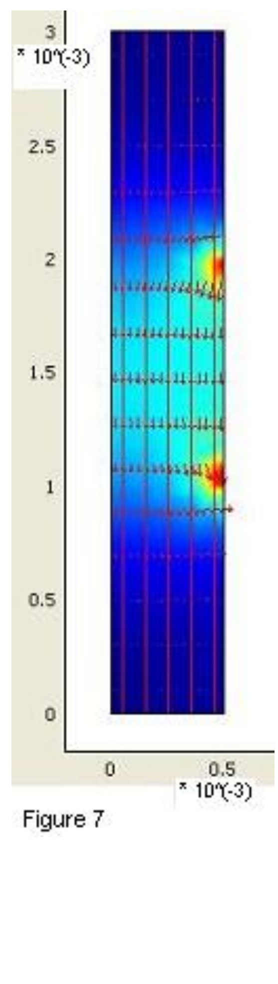


Figure 7

In addition to information about the velocity field, this model can show the distribution of species within the cathode. Since we are using air as oxygen source for the cathode, the three main species within the cathode are oxygen, water, and nitrogen. It is important to know the oxygen concentration to determine if concentration will be a limiting factor upon the reaction rate. If the concentration of oxygen becomes a limiting factor within the cathode, it is possible to supply purified O_2 rather than air to the cathode. Concentrations can also be important in determining poisoning of the cathodic electrode, for example poisoning due to CO from the air.

Models of the cathode can also determine whether the path and velocity of species could be improved. For example, whether the water byproduct is efficiently removed from the cathode. Figure 8 shows the oxygen mass fraction profile at five different x-values across the cathode. As expected, the oxygen concentration is highest toward the inlet, where the oxygen enters the cathode. Figure 9 shows the placement of the five x-values with red bars, the velocity field with arrows, and the oxygen mass fraction values by the coloration of the surface.

Figure 8

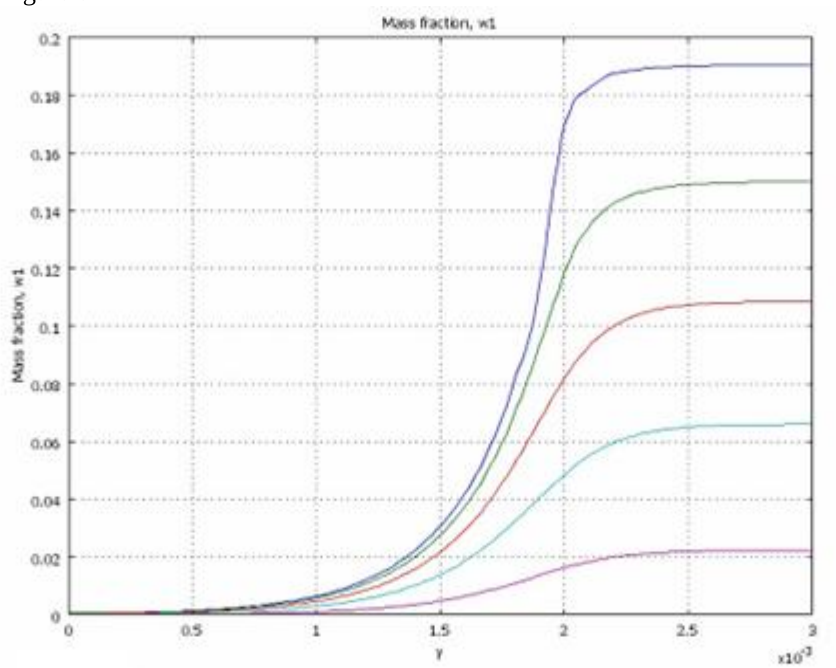


Figure 9

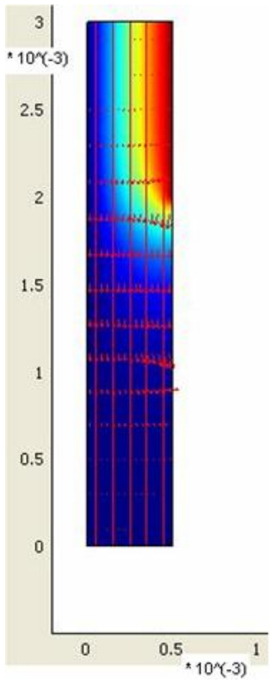


Figure 10 shows the water mass fraction profile through at five different x-values across the cathode. As one would expect, the concentration of water decreases near the oxygen inlet where air is the predominant species. Figure 11 depicts the placement of the Figure 10 profile with red bars, shows the velocity field with arrows, and portrays the water mass fraction values by the coloration of the surface.

Figure 10

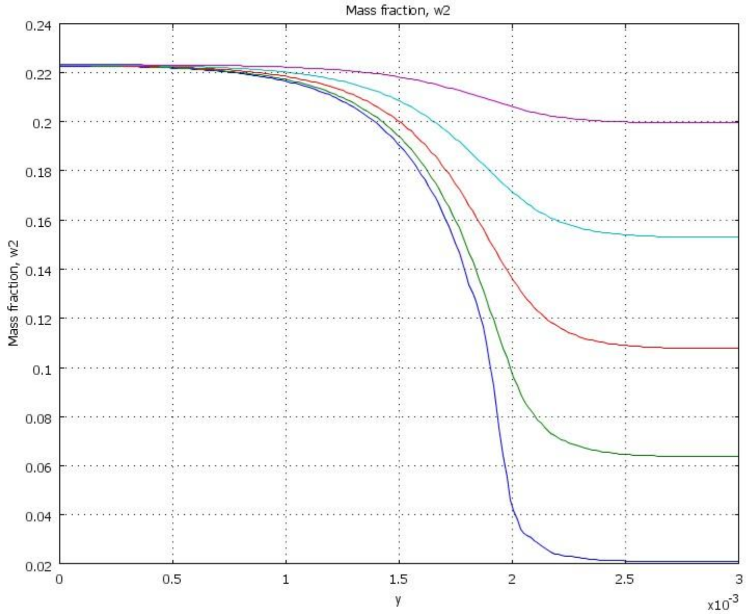
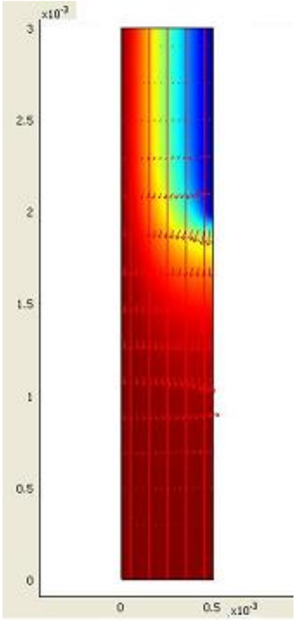


Figure 11



Validation

Since the parameters for this paper's ComSol model were primarily taken from the work of Yi and Nguyen [11], the validation will compare the results of Yi and Nguyen to the results of the ComSol model. Figure 2 shows an image of the cathode orientation used in the work of Yi and Nguyen. Note that the model's orientation is rotated from the orientation of the cathode model given in this paper, so x- and y-axes are reversed. The inlet/outlet positions are also reversed. As a consequence, the positive x-direction and y-direction in the work of Yi and Nguyen are typically negative y-direction and x-direction in this model. These differences are important to keep in mind when comparing the results of Yi and Nguyen to the results of the cathode model given in this paper.

As can be seen by comparing the two columns in Table 3, the overall shape of the graphs is duplicated in both models. In the pressure graphs, pressure nearest the inlet/outlet side of the cathode has an almost constant, high pressure along the inlet. The pressure rapidly drops to the fairly constant level of pressure at the outlet. Along the side where the membrane meets the cathode, the changes in pressure are less dramatic but follow the same trend. Due to the difference in location of the inlet and outlet, the oxygen mass fraction graphs from both models can be seen to be similar, but one is the symmetric image of the other. Due to the difference in location of the inlet and outlet and the rotation of the Yi and Nguyen model to obtain the model given in this paper, both the x- and y-axes are interchanged as are the negative and positive directions. As a result of these factors, the two images shown for velocity appear to match precisely. The magnitudes given in the Yi and Nguyen graphs are comparable to the magnitudes found using the ComSol model. The magnitudes of pressure can be seen to match exactly, and all of the same patterns are followed in the two sets of graphs.

Table 3

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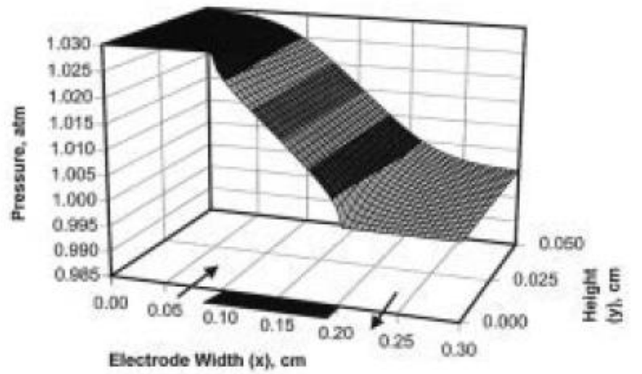
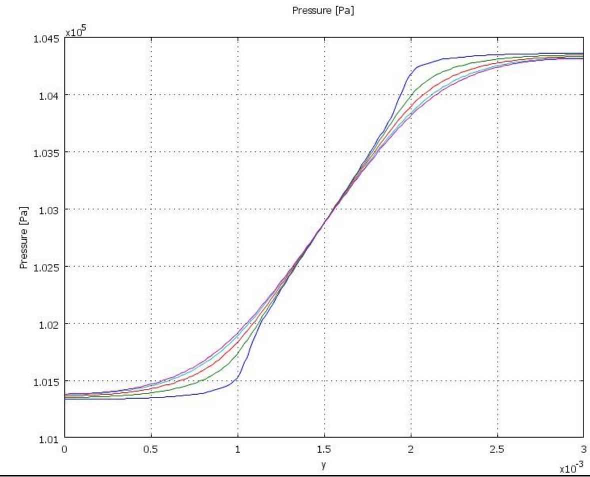
<tr><td>Yi and Nguyen-Pressure [11]</td><td>This Model-Pressure</td></tr>
<tr><td>
</td><td>
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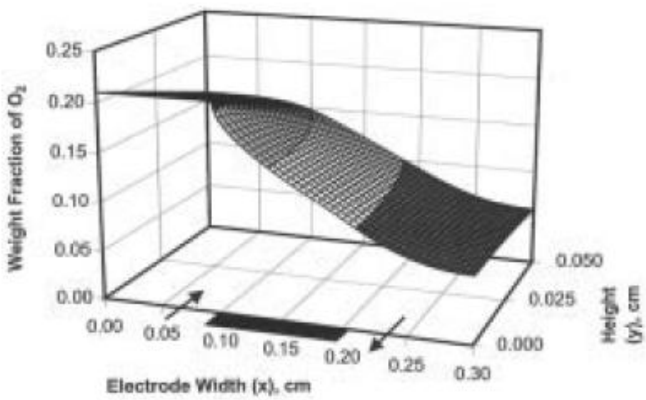
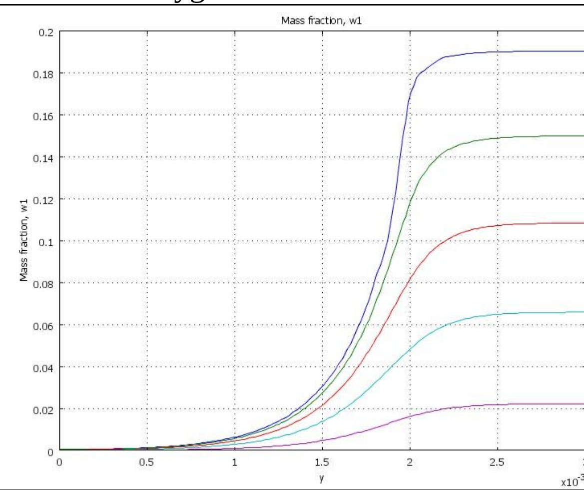
<tr><td>Yi and Nguyen-Oxygen Mass Fraction [11]</td><td>This Model- Oxygen Mass Fraction</td></tr>
<tr><td>
</td><td>
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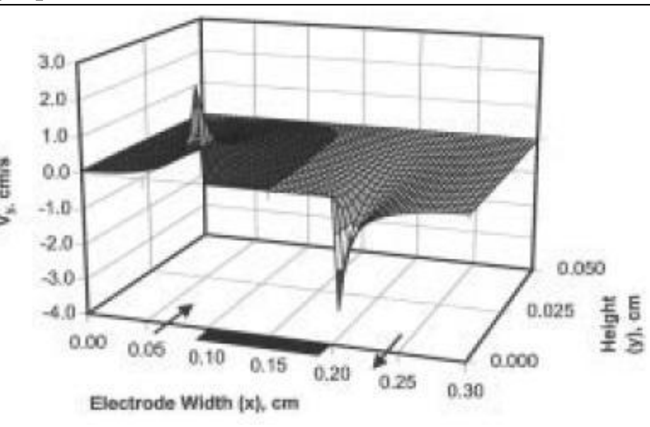
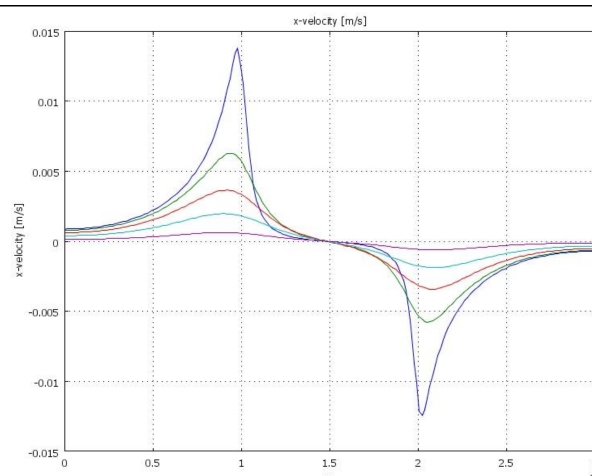
<tr><td>Yi and Nguyen-Y-direction Velocity Distribution [11]</td><td>This Model- X-direction Velocity Distribution</td></tr>
<tr><td>
</td><td>
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Additional validation can be found by comparing the velocity distribution field of He *et al.* [22] with the ComSol velocity distribution field. He *et al.* used the same model for their cathode as that used in the work of Yi and Nguyen (Figure 2) [11]. Figure 12 [22] shows the velocity distribution given by He *et al.*, where the inlet is on the left and the outlet is on the right. Figure 13 shows the velocity distribution field of this model where the inlet is at the top and the outlet is at the bottom.

Figure 13

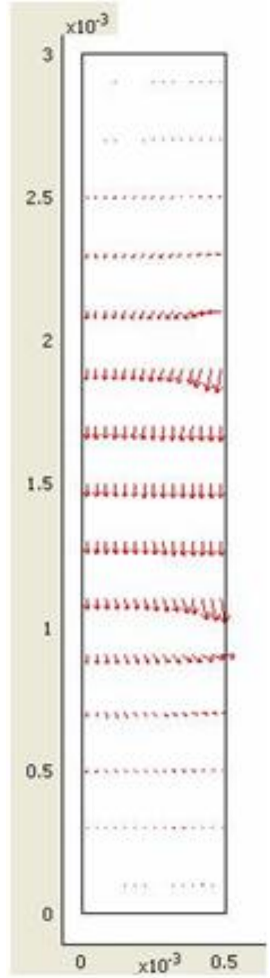
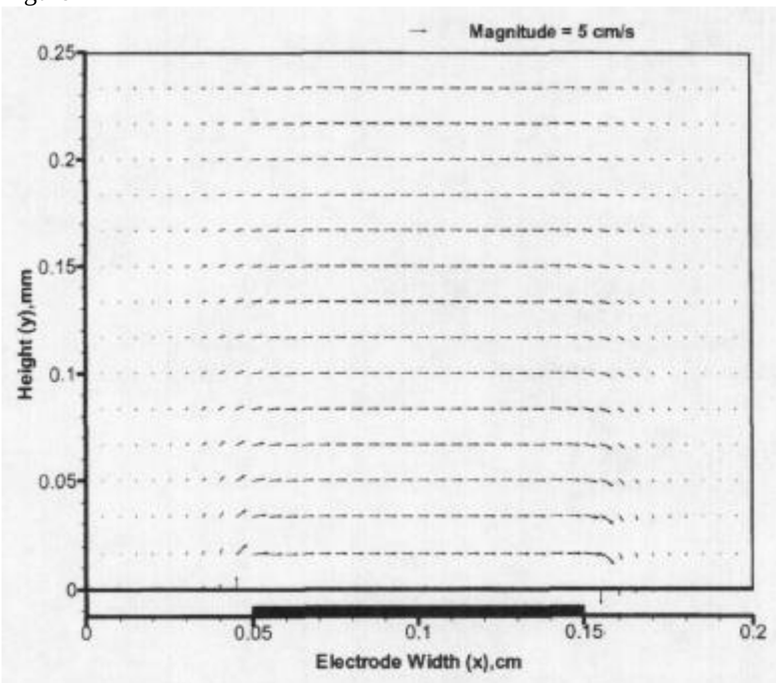


Figure 12



Parametric Study

One of the debatable factors when designing a PEM fuel cell system is whether to use pure oxygen supply or simply to pump air from the atmosphere into the fuel cell. Using air from the atmosphere is, of course, cheaper, both with respect to supply and with respect to minimizing energy costs. However, using pure oxygen supply maximizes the oxygen supply to the cathode and helps to prevent carbon monoxide poisoning of the expensive platinum or platinum based electrodes [23].

The ratio of oxygen to hydrogen within the cathode must be optimized. If the ratio of air or oxygen is too high, the gas can cause the polymer electrolyte membrane to dry out, decreasing the power output. If the ratio of air or oxygen is too low, the lack of oxygen at the reaction surface (the area of the cathode bordering the polymer electrolyte membrane) might reduce the reaction rate, decreasing the power output of the cell. The necessary mole fraction of oxygen depends upon the hydrogen source flow rate and the hydrogen molar content of the feed to the anode, so a model of the anode would also be necessary to determine the optimal oxygen feed concentration and flow rate. Since either pure hydrogen or a hydrocarbon can be supplied to the anode as a source of hydrogen, the necessary oxygen would depend upon the type of hydrogen supply used. In addition, carbon monoxide poisoning is more problematic when hydrocarbons are supplied to the anode, so pure oxygen would be more useful in helping to prevent poisoning if hydrocarbons are the hydrogen source [23].

The choice between using pure oxygen and air as a feed to the cathode is complex, but, in addition to providing other information, modeling can help determine the mass fraction of oxygen available at the polymer electrolyte membrane. Figures 14 and 15 depict the oxygen mass fraction at the cathode's boarder with the polymer electrolyte membrane. Figure 14 uses the oxygen content of air. Figure 15 is the available oxygen if the cathodic feed is pure oxygen. The shape of the curve is the same, but the oxygen mass fraction peaks at 4.8×10^{-10} for the air feed and at 2.4×10^{-9} for the pure oxygen feed.

Figure 14

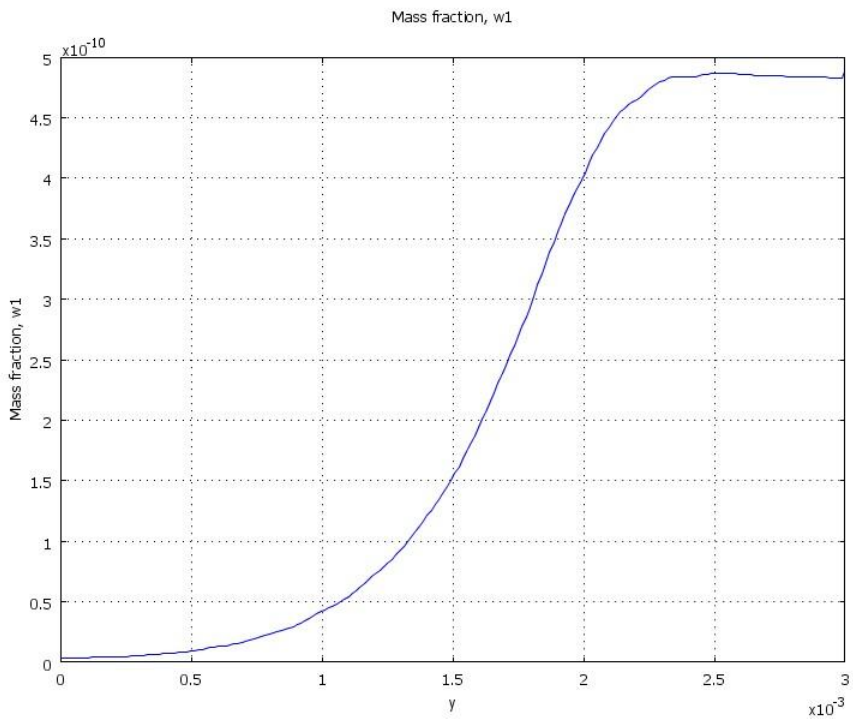
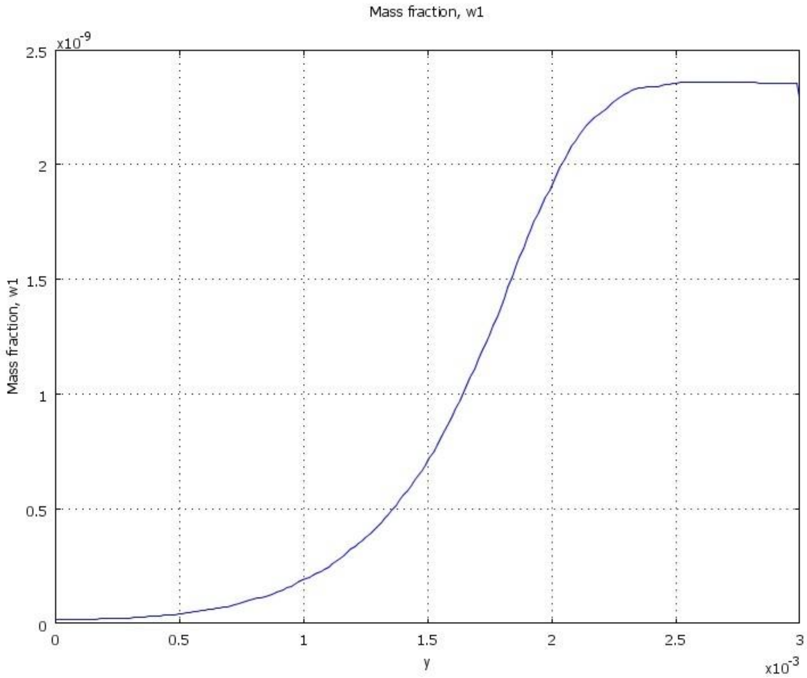


Figure 15



Conclusion

This model of a PEM cathode created using ComSol software can be seen to be in agreement with other published models of PEM fuel cells. Modeling the PEM fuel cell cathode can be valuable in determining the species distribution and flow path through the cathode. This model can provide valuable information on how modifications to the cathode would effect the oxygen concentration available at the interface with the membrane. This model could also show the effect of modifications upon the velocity field and pressure within the system. Changes in temperature, pressure, and porosity would be easily modeled and their effects could be determined without the use of valuable materials and labor.

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