

# **Compact Transient Model to Predict Water Concentration, Temperature, Potential and Pressure Across Nafion Membranes**

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## **Abstract**

A numerical model was developed to predict the water concentration, temperature, potential and pressure across a Nafion membrane used in proton exchange membrane (PEM) based fuel cells. The numerical model consists of simultaneously calculating the diffusive flux for water and hydrogen, the proton potential and the pressure and temperature at each node.

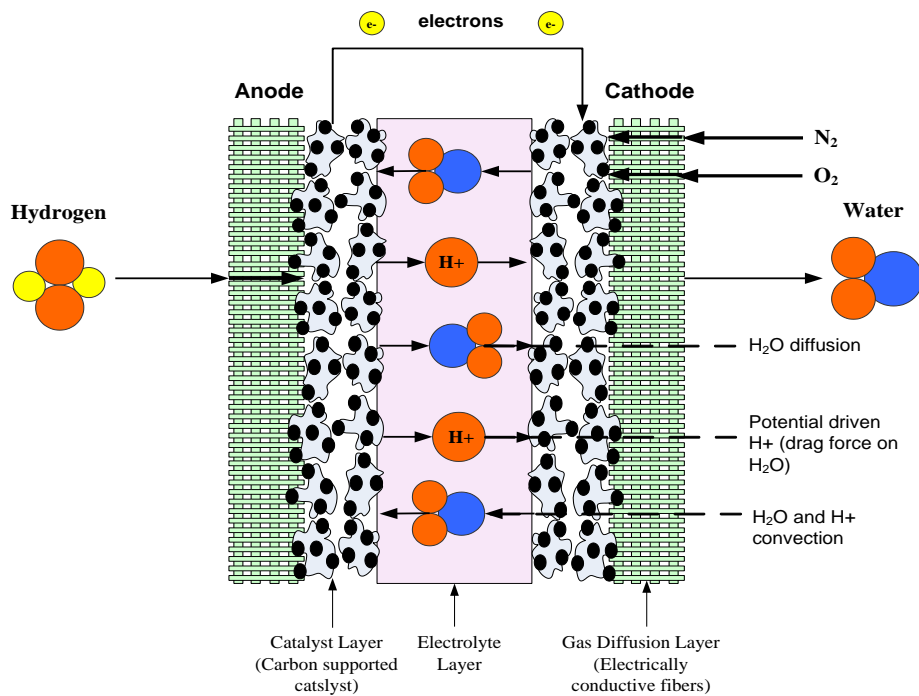
**Keywords:** Proton exchange membrane fuel cell; Nafion membrane

## **1 Introduction**

In proton exchange membrane fuel cells (PEMFC), the fuel travels to the catalyst layer, and is decomposed into protons ( $H^+$ ) and electrons. The electrons travel to the external circuit to power the load, and the hydrogen protons travel through the electrolyte until they reach the cathode to combine with oxygen to form water. The electrolyte layer is essential for a fuel cell to work properly. The PEMFC electrolyte must provide high ionic

conductivity, present an adequate barrier to the reactants, be chemically and mechanically stable, have low electronic conductivity, be easily manufactured and preferably low-cost.

The polymer electrolyte membrane contains water and hydrogen protons; therefore, the transfer of the water and protons transfer are important phenomena to investigate [1-10]. In addition to species transfer, the primary phenomena investigated inside the membrane are energy transfer and potential conservation [9]. For water transport, the principle driving forces modeled are a convective force, an osmotic force (i.e. diffusion), and an electric force [1-10]. The first of these results is from a pressure gradient, the second from a concentration gradient, and the third from the migration of protons from anode to cathode and their effect (drag) on the dipole water molecules. Proton transport is described as a protonic current and consists of this proton driven flux and a convective flux due to the pressure driven flow of water in the membrane [1-10]. Figure 1 illustrates the transport phenomena for the protons taking place within the membrane.



## Figure 1: Membrane Transport Phenomena

Most membrane models in the literature are isothermal, and therefore, unsuitable for water and heat management studies. A relatively small number of models include non-isothermal effects [7, 12, 13, 15, 16], and typically, the ones that do focus on modeling multiple fuel cell layers, with simplifying assumptions for the membrane layer. Also, many models that do allow for operating temperature changes, but not a temperature gradient. For most conditions, the change in parameter values with temperature has a more significant impact than accounting for temperature gradients, although the two are coupled to a certain extent.

Transient models examine changes in potential and transport phenomena (flow rates, water production and current density). These models are aimed at examining different load requirements. Most models do not examine transients due to the computational cost and complexity. Some codes in the literature can take on the order of tens of minutes in certain circumstances [24]. One of the first models to examine transients in PEM fuel cells is a stack-level model by Amphlett et al. [20]. This is an empirical model that examines temperature and gas flow rates. There have been some more complex transient models that have examined the behavior of water content in the membrane that have demonstrated the effects of the membrane drying out [10, 21]. Other transient models have either not included liquid water, do not report transient results or focus mainly on water transport in the gas diffusion layers [15, 16, 17, 18, 19, 20, 22]. There are no results reported in the literature that simultaneously show the temperature, potential, water

concentration and pressure profile in the membrane based upon varying current densities, temperatures and pressure gradients.

The model presented in this paper is a compact model that can simultaneously calculate the temperature, pressure water concentration and potential at a user-specified number of positions through the membrane. Since the code uses built-in MATLAB functions, it is only a few hundred lines, can compute hundreds of points within the membrane within seconds, can easily be expanded to include additional transient boundary conditions and can be easily integrated into an overall fuel cell model.

Proton exchange membrane fuel cell (PEMFC) models are necessary to predict fuel cell performance to optimize performance to help reduce development costs and time. Water management is critical for efficient fuel cells due to its large effect on ohmic and mass-transport overpotentials, operating conditions and membrane electrode assembly design.

Since the membrane is the key element in a fuel cell, a lot of attention has been focused on it in terms of modeling. In the literature, there are both macroscopic and microscopic models. The microscopic models focus on single ions, and pore-level effects, and the macroscopic models are typically more empirical and focus on the transport phenomena. Although the microscopic models reveal valuable information about what occurs in the membrane, they are generally too complex to use in an overall fuel cell model. The membrane system is assumed to consist of three main components: the membrane, protons and water.

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Most models of the polymer exchange membrane are overly complicated. Many secondary effects are often included, such as convective (Darcy) water flow, membrane swelling and other membrane properties that are dependent upon water content. Simple models are desirable due to reduced model development time; reduce computational time, and easy integration into other models.

## **1.1 Literature review**

Current fuel cell modeling focuses on effects with specific designs and materials. Verbrugge and Hill [1] and Bernari and Verbrugge [2] developed a steady-state, isothermal, one-dimensional model for the electrochemical performance in a PEMFC. They claim that the liquid and gas pressure evolve separately in the GDL layer, which implies that they are not at equilibrium with each other. This model only applies to fully hydrated membranes, and the drag flux due on the water molecules is not considered.

Springer, Zawodzinski and Gottesfeld [3] presented a 1D, steady-state isothermal model of a PEMFC with emphasis on water transport phenomena through a Nafion membrane. An improved model with a detailed treatment of ion transport and ionic conductivity in the catalyst and backing layer was developed in [4]. This model predicted the mass

transport limitations at high current densities. In [5], Springer, Zawodzinski, Wilson and Gottesfeld provide experimental and theoretical results for unsteady-state effects in a 1-D isothermal PEMFC stack. They use a frequency diagram to quantify the specific influences of several sources of losses such as activity in the cathode and conductivity of the catalyst layer and the membrane.

Weisbrod, Grot, and Vanderborgh [6] developed a through the electrode model to predict fuel cell performance as a function of water balance in the channels, and across the membrane. The model predicts the influence of both the catalyst layer thickness, and its Platinum catalyst loading.

Nyguyen and White [7] developed a 1-D, steady-state water and heat management model for PEMFCs. This model does not study the details of the membrane and the catalyst layers separately since it models that entire electrode as one unit. It does steady the affect of humidification levels and their effect on fuel cell performance. This model was enhanced in [8], with the addition of a linear model for the membrane, and then a 2-D, steady-state model for multispecies transport in the electrodes. This model studies the effect of an interdigitated gas distributor on PEMFC performance. However, it was unable to predict the effect of liquid water within the system. Thirumalai and White [9] used the model developed in [8] to predict the operating parameters, flow field design and gas manifold geometry on the performance of the fuel cell stack.

Van Bussel, Koene and Mallant [10] create a 2D dynamic model, with a 1D model through the membrane. The model is based upon the work of Springer et al. [3], but uses experimental data from Hinatsu, Mizhuta and Takenaka [11]. The model showed that

current density can vary strongly along the gas channels, especially when operating with dry gases.

Gurau, Kakac, and Lui [12] developed a 2-D non-isothermal model. They considered the gas channel, and the diffuser-catalyst layer a single entity. The model shows a non-uniform, reactant distribution has an important impact on the current density distribution. This model is based upon an infinitely thin catalyst layer, which is unable to predict the voltage due to transport limitations in the catalyst layer.

Fuller and Newmann [13] and Weber and Newmann [14] developed a steady-state, 2-D model for the membrane electrode assembly. Unlike other models, concentration solution theory was used. They argued that water was produced in the gaseous phase at the catalyst surfaces. Their model is valid if there is no condensation within the catalyst layer.

The remainder of this paper is organized as follows: In Section 2, the proposed model is derived from the basic cell parameters. Section 3 details the numerical implementation of the model, while Section 4 presents the results and the associated discussions. The conclusions are drawn in Section 5.

## **2 The Proposed Model**

Figure 1 shows a membrane with water and proton flow in the region  $0 < y < N$ . As in all earlier papers on transport phenomena in the membrane, the hydrogen protons are

constant. Conservation equations are required for the water, protons, energy and potential.

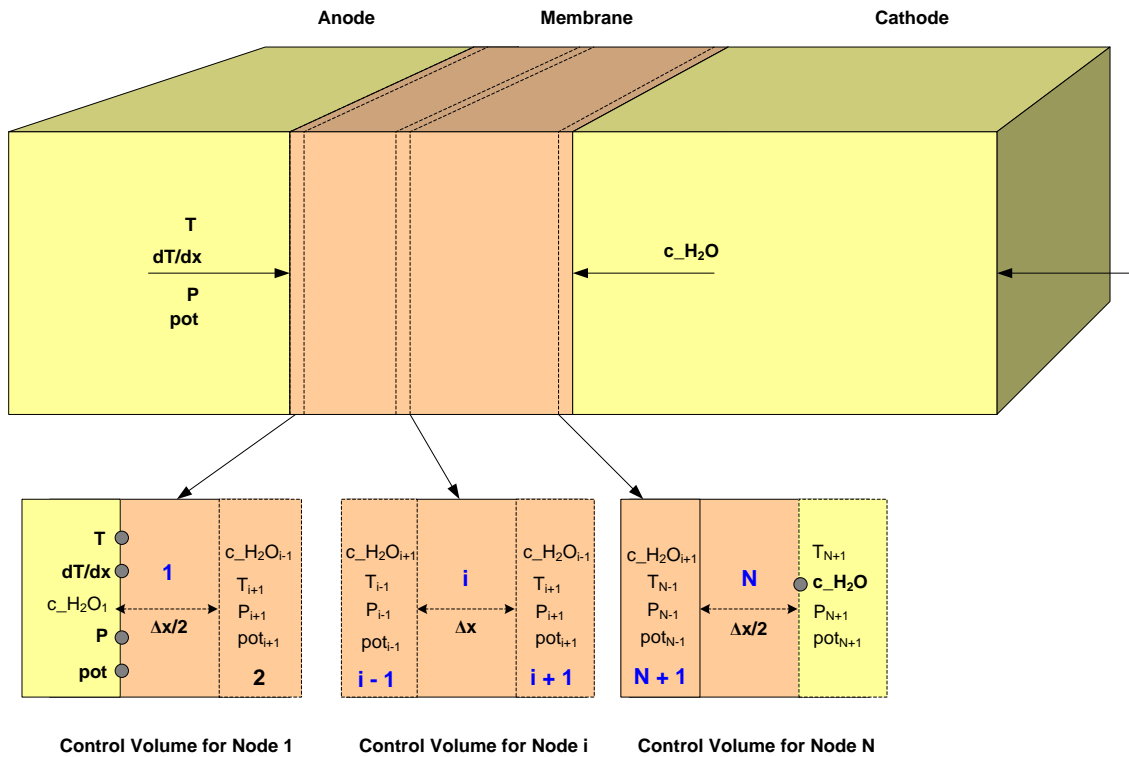


Figure 2 Slices created for 1-D membrane model

The main assumptions include the following: rate limiting water diffusion in the Nafion membrane, steady state, water diffusion perpendicular to the membrane surface (membrane thickness is much smaller than the channel length), constant pressure along the channels, constant concentration in the gas stream at any given location along the channel (plug flow behavior), constant temperature, ideal gas behavior, negligible gas diffusion through the membrane, negligible pressure drop across the membrane (no permeation through the membrane), membrane properties independent of water content



(diffusion coefficient and membrane thickness), equilibrium between channel and membrane interfaces, and linear relationship between membrane water content and channel water concentration (analogous to Henry's law).

## **2.1 Mass and Species Conservation**

When modeling the polymer electrolyte membrane, it is typically assumed that the concentration of positive ions is fixed by electroneutrality, which means that a proton occupies every fixed  $\text{SO}_3^-$  charge site. The charge sites are assumed to be distributed homogeneously throughout the membrane, which results in a constant proton concentration in the membrane. A flux of protons, thus, results from a potential gradient and not a concentration gradient. In addition, the number of protons that can be transported is only one, which helps to simplify the governing transport equations. Most papers use overall mass balances to account for the protons and water at the membrane/catalyst interface [3], or the Nernst-Planck equation for each species [1].

For both water and protons, the mass conservation equation can be represented as:

$$\frac{\partial c_i}{\partial t} = -\frac{\partial}{\partial t} N_i \quad (1)$$

where  $i$  is a subscript used to denote either water ( $\text{H}_2\text{O}$ ) or protons ( $\text{H}^+$ );  $c_i$  is the molar concentration, and  $N_i$  is the molar flux due to electro-osmotic driving forces and

convection. In a diluted solution,  $N_i$  is given by the Nernst-Planck equation along with the Nernst-Einstein relationship:

$$N_i = J_i + c_i u^m \quad (2)$$

where  $u^m$  is the mixture velocity and  $J_i$  is the diffusive flux.

Therefore, the mass conservation of water is:

$$\frac{\partial c_{H_2O}^m}{\partial t} = -\frac{\partial}{\partial x} J_{H_2O} - \frac{\partial}{\partial x} (c_{H_2O}^m u^m) \quad (3)$$

When  $\frac{\partial c_{H_2O}^m}{\partial t} = 0$ , since  $\frac{\partial}{\partial x} J_{H_2O} = -\frac{\partial}{\partial x} (c_{H_2O}^m u^m)$

The diffusive flux for water will be used in the following paragraphs to calculate the water concentration:

$$J_{H_2O} = -D_{c_{H_2O},T} \frac{\partial c_{H_2O}^m}{\partial x} + 2.5 \frac{\lambda_{H_2O/SO_3}}{22} \frac{i_{mx}}{F} \quad (4)$$

From which we obtain:

$$\frac{\partial c_{H_2O}^m}{\partial x} = \frac{J_{H_2O}}{-D_{c_{H_2O},T}} + \frac{2.5}{D_{c_{H_2O},T}} \frac{\lambda_{H_2O/SO_3}}{22} \frac{i_{mx}}{F} \quad (5)$$

In polymer electrolyte membrane fuel cells, the two important fluxes or material balances are the proton flux and the water flux. The membrane needs to stay hydrated to ionically conduct hydrogen; therefore, the water profile must be calculated in the electrolyte. In the Nafion membrane, two types of water flux are present: back diffusion and electroosmotic drag.

Both fluxes can be accounted for by the following equation:

$$J_{H_2O}^M = -D_{cH_2O,T} \frac{\partial c_{H_2O}^m}{\partial x} + n_{drag} \frac{i_x}{F} \quad (6)$$

where  $n_{drag}$  is the measured drag coefficient,  $i_x$  is the protonic current in the  $x$  direction,  $F$  is Faradays constant,  $\lambda_{H_2O/SO_3}$  is the water content (molH<sub>2</sub>O/molSO<sub>3</sub><sup>-</sup>),  $\rho_{dry}^m$  is the dry membrane density (kg/m<sup>3</sup>),  $D_{cH_2O,T}$  is the diffusion coefficient and  $M^m$  is the membrane molecular mass (kg/mol). The water content is not constant in this equation. The resistance of the electrolyte can be estimated using the water content, which can be described by:

$$n_{drag} = 2.5 \frac{\lambda_{H_2O/SO_3}}{22} \quad (7)$$

$$\lambda_{H_2O/SO_3} = \frac{c_{H_2O}^m}{\frac{\rho_{dry}^m}{M^m} - b c_{H_2O}^m} \quad (8)$$

where  $b$  is the membrane extension coefficient in the  $x$  direction, which is determined experimentally, and the value is typically used.

$D_{c_{H_2O},T}$  is the diffusion coefficient which includes a correction for the temperature and for the water content it is expressed in a fixed coordinate system with the dry membrane by:

$$D_{c_{H_2O},I} = D' e^{2416 \left( \frac{1}{303} - \frac{1}{T} \right)} \frac{\lambda_{H_2O/SO_3}}{a(17.81 - 78.9a + 108a^2)} \quad (9)$$

where  $a$  is the activity of water, and  $D'$  (m<sup>2</sup>/s) is the diffusion coefficient measured at constant temperature and in coordinates moving with the swelling of the membrane.  $D'$  has been added to the above equation to ensure that water contents below 1.23 do not result in negative diffusion coefficients.  $D'$  at 30 °C is written as:

$$D = \begin{cases} 2.642276 \times 10^{-13} \lambda_{H_2O/SO_3} & \lambda_{H_2O/SO_3} \leq 1.23 \\ 7.75 \times 10^{-11} \lambda_{H_2O/SO_3} - 9.5 \times 10^{-11} & 1.23 < \lambda_{H_2O/SO_3} \leq 6 \\ 2.5625 \times 10^{-11} \lambda_{H_2O/SO_3} - 2.1625 \times 10^{-10} & 6 < \lambda_{H_2O/SO_3} \leq 14 \end{cases} \quad (10) \text{ for}$$

The total molar flux for water can be expressed as:

$$N_{H_2O} = J_{H_2O} + (c_{H_2O}^m u^m) \quad (11)$$

where the mixture velocity  $u^m$  is given by the momentum equation below.

The mass conservation of water can be expressed as:

$$\frac{\partial c_{H_2O}^m}{\partial t} = -\frac{\partial}{\partial x} J_{H_2O} + -\frac{\partial}{\partial x} (c_{H_2O}^m u^m) \quad (12)$$

where the mixture velocity  $u^m$  is given by the momentum equation.

Now, due to the assumption of electroneutrality and the homogeneous distribution of charge sites, the mass conservation of protons simplifies to:

$$\frac{\partial c_{H^+}}{\partial x} = 0, \& \frac{\partial c_{H^+}}{\partial t} = 0 \quad (13)$$

Thus, as soon as a current exists, the membrane is charged; and the concentration of protons remain constant. The charge of the protons equals that of the fixed charges. The diffusive molar flux for the protons ( $J_{H^+}$  can, therefore, be written as:

$$J_{H^+} = -\frac{F}{RT} D_{H^+} c_{H^+} \frac{\partial \Phi_m}{\partial x} \quad (14)$$

Where  $\Phi_m$  is the membrane proton potential and  $D_{H^+}$  is the proton diffusivity. Combining this diffusive flux with the convective flux results in the total molar flux for the hydrogen protons, i.e.:

$$N_{H^+} = J_{H^+} + c_{H^+} u^m \quad (15)$$

## 2.2 Momentum Equation

For the mixture (water and protons), the assumption is made that the momentum equation takes the form of the generalized Darcy relation [??]:

$$u^m = -\frac{Kk_r^s}{\mu} \left[ \frac{\partial p}{\partial x} - \rho g \cos \theta \right] \quad (16)$$

where  $K$  is the absolute permeability of the porous medium,  $k_r^s$  is the relative permeability,  $g$  is the gravity, and  $\theta$  is the angle that the x-axis (the direction of flow) makes to the direction of gravity,  $\rho$  is the mixture density given by:

$$\rho = M_{H^+} c_{H^+} + M_{H_2O} c_{H_2O} \quad (17)$$

and  $\mu$  is the dynamic viscosity of the mixture given by:

$$\mu = \frac{M_{H^+} c_{H^+}}{\rho} \mu_{H^+} + \frac{M_{H_2O} c_{H_2O}}{\rho} \mu_{H_2O} \quad (18)$$

### 2.3 Conservation of Energy Equation

Energy is transported by conduction and convection within the three phases of the membrane (polymer, liquid/gas). The effects of Ohmic losses within the membrane are considered by an additional source term in the energy balance equation so that energy conservation is given by:

$$\rho c_p \frac{\partial T}{\partial t} = \lambda_m \frac{\partial^2 T}{\partial x^2} - M c_p N \frac{\partial T}{\partial x} + R_m \quad (19)$$

$$\frac{\partial^2 T}{\partial x^2} = \frac{M c_p N}{\lambda_m} \frac{\partial T}{\partial x} - \frac{R_m}{\lambda_m}$$

Rewritten as:

$$\lambda_m T'' - M c_p N T' = -R_m$$

$$(T)' - T' = 0$$

where

$$\rho c_p = \rho_m^{dry} c_{pm} + \rho_{H_2O}^m c_{pH_2O}^m + \rho_{H^+} c_{pH^+} \quad (20)$$

Substituting,

$$\rho_{H^+} = M_{H^+} c_{H^+} \quad \& \quad \rho_{H_2O}^m = M_{H_2O} c_{H_2O}^m \quad (21)$$

$$M c_p N = M_{H_2O} c_{p,H_2O}^m N_{H_2O} + M_{H^+} c_{p,H^+} N_{H^+} \quad (22)$$

The transient energy effect associated with mass storage within the hydrated membrane is neglected because the dry membrane mass does not change and is several orders of magnitude larger than that of the water which hydrates the membrane.

Substituting the expressions for  $N_{H_2O}$  and  $N_{H^+}$ , from equations (11) and (15) respectively, an expanded expression for  $Mc_p N$  can be obtained:

$$Mc_p N = M_{H_2O} c_{p,H_2O}^m \left( c_{H_2O}^m u^m - D_{c_{H_2O},T} \frac{\partial c_{p,H_2O}^m}{\partial x} + \frac{2.5 \lambda_{H_2O/SO_3}}{22} \frac{i_m}{F} \right) + M_{H^+} c_{p,H^+} \left( c_{H^+} u^m - D_{H^+} c_{H^+} \frac{\partial \Phi_m}{\partial x} \right) \quad (23)$$

The source term,  $R_m$ , is given by

$$R_m = \frac{i^2}{\sigma_m} \quad (24)$$

where  $\sigma_m$  is the conductivity of the membrane. It is a function of the temperature and the water content and is given by:

$$\sigma_m = \sigma_{m303} e^{1268 \left( \frac{1}{303} - \frac{1}{T} \right)} \quad (25)$$

with  $\sigma_{m303}$ , the conductivity of the membrane at 303 K given by:

$$\sigma_{m303} = 0.5139 \lambda_{H_2O/SO_3} - 0.326 \quad \text{for } \lambda_{H_2O/SO_3} > 1 \quad (26)$$

## 2.4 Ohm's Law

The equation for the proton potential is derived from Ohm's law. Both terms represent the proton flux divided by the membrane conductivity. The electroneutrality assumption allows the total molar proton flux to be related directly to current density and results in

the first term. The second term containing  $u^m$  represents the convective flux of protons.

Combined they result in the following equation:

$$\frac{\partial \Phi_m}{\partial x} = -\frac{i}{\sigma_m} + \frac{F}{\sigma_m} c_{H^+} u^m \quad (27)$$

## 2.5 Mixture Pressure Relation

Most models in the literature assume only concentration gradients, and not pressure gradients [3]. A pressure drop can occur if the anode and cathode pressure are different.

The mixture pressure gradient is assumed to behave linearly between the anode and cathode interfaces so that [2]:

$$\frac{dp}{dx} = \frac{p_+ - p_-}{\delta} \quad (28)$$

Where  $p_+$  and  $p_-$  are the pressures at the anode/membrane and cathode/membrane interface, and  $\delta$  is the thickness. At the interface with the anode catalyst layer, the mixture pressure is assumed equal to that of the gas pressure under the assumption that no liquid is present. At the cathode catalyst interface, it is assumed that the mixture pressure can be approximated by

a linear relation and the liquid pressure weighted by the saturation ratios (the volume ratio of liquid water to gaseous water in the pores of the catalyst layer). For the results generated, the saturation ratio was set to zero, therefore there was no effect of liquid pressure on the pressure gradient.



## 2.6 Membrane Water Activity Relation

The relation for the water activity within the membrane is given by the reciprocal of the sorption curve. As with the water vapor activity at the interfaces, the results from Springer et al. [3] for water vapor activity in Nafion 117 at 30 °C is given by:

$$a = \begin{cases} \left( \frac{c_1}{2160} + c_2 \lambda_{H_2O/SO_3} + 216 \sqrt{c_3 - c_4 \lambda_{H_2O/SO_3} + c_5 \lambda_{H_2O/SO_3}^2} \right)^{1/3} \\ - \frac{134183}{2160} \left( c_1 + c_2 \lambda_{H_2O/SO_3} + 216 \sqrt{c_3 - c_4 \lambda_{H_2O/SO_3} + c_5 \lambda_{H_2O/SO_3}^2} \right)^{1/3} & \lambda_{H_2O/SO_3} \leq 14 \\ + \frac{797}{2160} \\ 0.7143 \lambda_{H_2O/SO_3} - 9.0021 & 14 \leq \lambda_{H_2O/SO_3} \leq 16.8 \\ 3 & 16.8 \leq \lambda_{H_2O/SO_3} \end{cases}$$

## 2.7 Boundary conditions

The model is a one-dimensional model, and solves for the concentration of water, potential, temperature and pressure simultaneously. To solve for these transient variables, initial and boundary conditions are required. At  $x = 0$ , three boundary conditions are necessary to fully specify the problem. These are:

$$c_{H_2O}^m(x_0) = b_0, \quad \frac{\partial c_{H_2O}^m(x_0)}{\partial x} = 0 \quad (30)$$

$$T(x_0) = b_1, \quad \frac{\partial T(x_0)}{\partial x} = b_2 \quad (31)$$

$$\Phi_m(x_0) = b_3, \quad \frac{\partial \Phi_m(x_0)}{\partial x} = 0 \quad (32)$$

$$P(x_0) = b_4, \quad \frac{\partial P(x_0)}{\partial x} = 0 \quad (33)$$

## 2.8 Interface Water Activity Relation

At the membrane interfaces, the water vapor activity is given by

$$a = \frac{RT}{p_{sat}(T)} c_{H_2O}^g + 2s \quad a \in [0,3] \quad (34)$$

where  $c_{H_2O}^g$  is the water vapor concentration and  $s$  is the saturation ratio.

$$p_{sat}(T) = -2846.4 + 411.24T - 10.554T^2 + 0.16636T^3 \quad (35)$$

This expression differs with respect to the one given in Springer et al. in that it defines activity as a function of water concentration and not pressure and attempts to relate saturation ratio to activity. Here an assumption is made that  $s$  is zero for activities less than 1, meaning that no liquid water is present in the membrane pores until the activity exceeds 1. The highest value that the first term can reach is 1; therefore, a maximum saturation ratio of 1 results in an activity of 3.

The water uptake is a function of activity, and can be expressed by:

$$\lambda_{H_2O/SO_3} = \begin{cases} 0.043 + 17.81a - 39.85a^2 + 36a^3 & a < 1 \\ 14 + 1.4(a - 1) & 1 \leq a \leq 3 \\ 16.8 & a \geq 3 \end{cases} \quad (36)$$

## 3 Numerical Implementation

The equations are solved using MATLAB using the `bvp4c` function to solve the boundary value problem for the ordinary differential equations.

The membrane and proton properties used for the membrane portion of the model are shown in Table 1.

**Table 1. Parameters Used for Membrane Layer**

Variable	Description	Value	Units
Outside Temperature	Temperature of fuel cell stack surroundings.	298	K
Outside pressure	Pressure of fuel cell stack surroundings.	101,325.01	Pa
<b>Proton Properties:</b>			
Initial proton concentration	Initial proton concentration	1.2e-3	mol/m <sup>3</sup>
Proton diffusivity	Proton diffusion coefficient	4.5e-5	cm <sup>2</sup> /s
<b>Membrane Properties:</b>			
Density of membrane	Density of membrane	2,000	kg/m <sup>3</sup>
Molecular weight of membrane	Molecular weight of membrane	1.1	Kg/mol SO <sub>3</sub>
Specific heat of membrane	Specific heat of membrane	852.63	J/kgK
Permeability	Permeability of membrane	1.8e-18	m <sup>2</sup>
Initial saturation ratio	Initial saturation ratio	0.02	N/A

`sol = bvp4c(odefun,bcfun,solinit)` integrates a system of ordinary differential equations of the form

$$y' = f(x, y)$$

on the interval  $[a, b]$  subject to two-point boundary value conditions:

$$0 = bc(y(a), y(b), p)$$

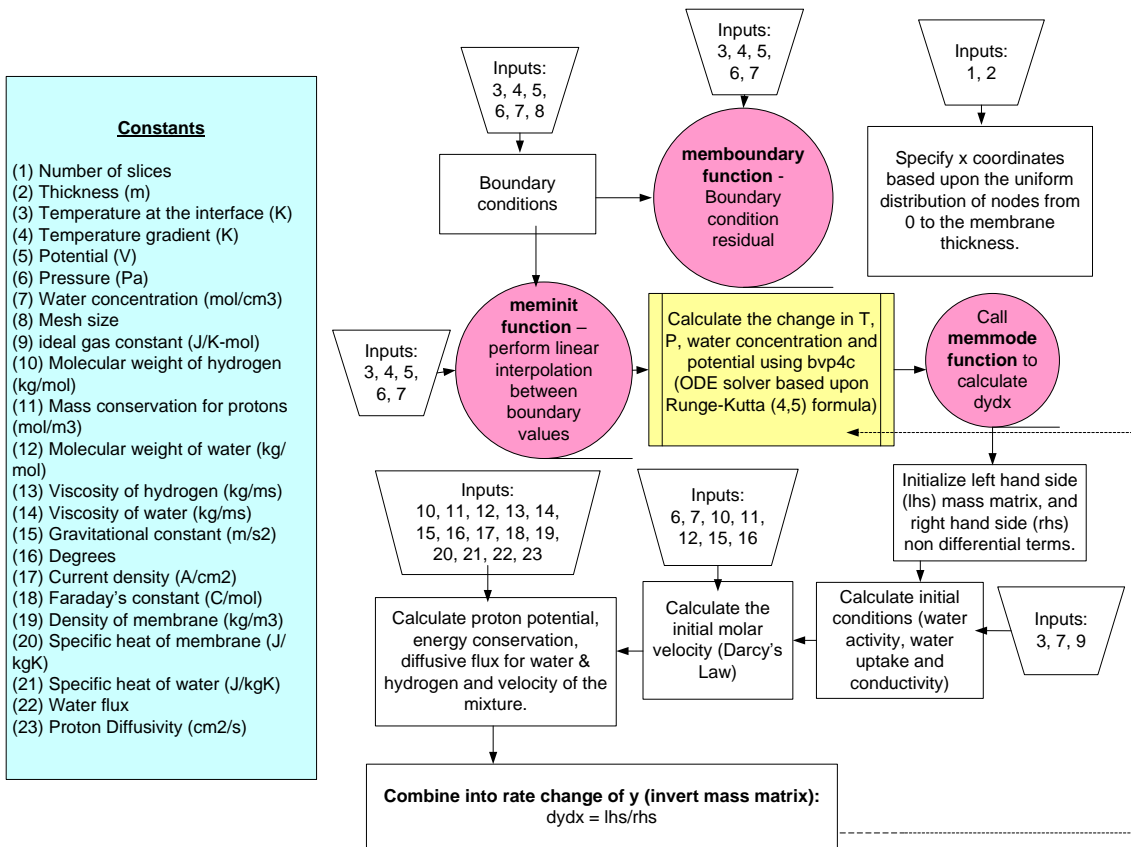
where  $p$  is the parameters. A two-point boundary value problem was created, with an initial guess using the built-in MATLAB function `bvpinit`:

$$\text{solinit} = \text{bvpinit}(x, \text{yinit})\text{cvv}$$

where  $x$  is a vector that specifies an initial mesh, where the mesh points are the number of points specified between  $x(1)$  and  $x(\text{end})$  by MATLAB's `linspace` function. A function is written as an initial condition adapter function as an input for `bvpinit` to perform linear

interpolation between boundary values and initialize the constant values to be equal to boundary conditions.

The two-point boundary point problem is solved using the `bvp4c` function, with the mass matrix of membrane equations, boundary constants, mesh size, `bvpinit` results and a function for the boundary conditions residuals. This function was written because at the solution we expect  $y(a) = bc\_a$ ,  $y(b) = bc\_b$  and `bc_a` and `bc_b` are row vectors and `ya`, `yb` are columns, so adapt.



**Figure. Flow chart of membrane model**

Since there are five differential equations for each state variable, a mass matrix in MATLAB will be used to efficiently solve the differential equations simultaneously. To set up the equations, first rewrite them with all the differentials on the left side and everything else on the right side. The equations will then be arranged into an order roughly matching the order of the state variables. The terms will then be collected together and put into a "Mass" matrix m-file which is a function of the state variables  $M(y)$ . The right-hand side forms the equations you compute in the  $dydx$  function  $f(x, y)$ . The resulting form of the equations is  $M(y) * dydx = f(x, y)$  where  $y$  is the state variables

and  $M$  and  $f$  are matrix functions. Use `odeset` to specify the mass m-file  $M(y)$  and then call one of the ode solvers.

The code allows input of any number of control volumes or “slices” per layer. For the uniform distribution of nodes, the location of each node ( $x_i$ ) is:

$$x_i = \frac{(i-1)}{(N-1)}L \quad \text{for } i = 1..N \quad (40)$$

where  $N$  is the number of nodes used for the simulation. The distance between adjacent nodes ( $\Delta x$ ) is:

$$\Delta x = \frac{L}{N-1} \quad (41)$$

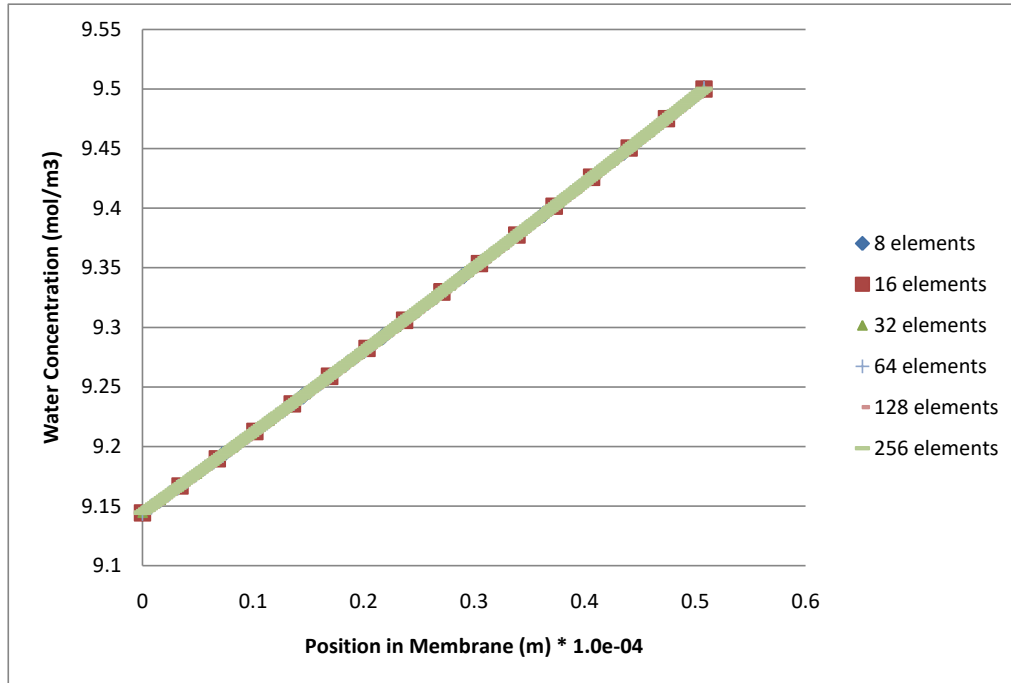
A control volume is defined around each node; the control surface bisects the distance between the nodes, as shown in Figure 2.

## 4 Results and Discussion

Within the membrane, water is transported because of a diffusive force, a convective force due to a pressure gradient and an electric drag force imposed on the water molecules by the charged protons moving from the anode to the cathode. The results presented were obtained using the parameters in Table 1. Of the most interest are the water concentration profiles.

## 4.1 Effect of Mesh Size

Figures compares the results for 8, 16, 32, 64, 128 and 256 element mesh sizes.



**Figure. Water Concentration vs. Position in membrane for 8, 16, 32, 64, 128 and 256 elements.**

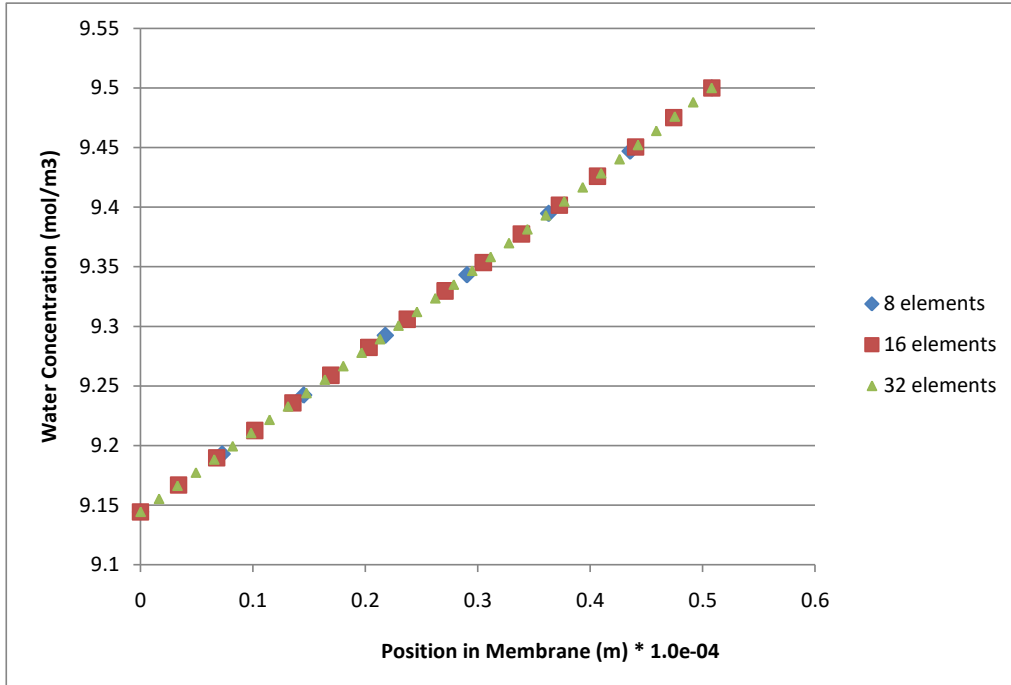
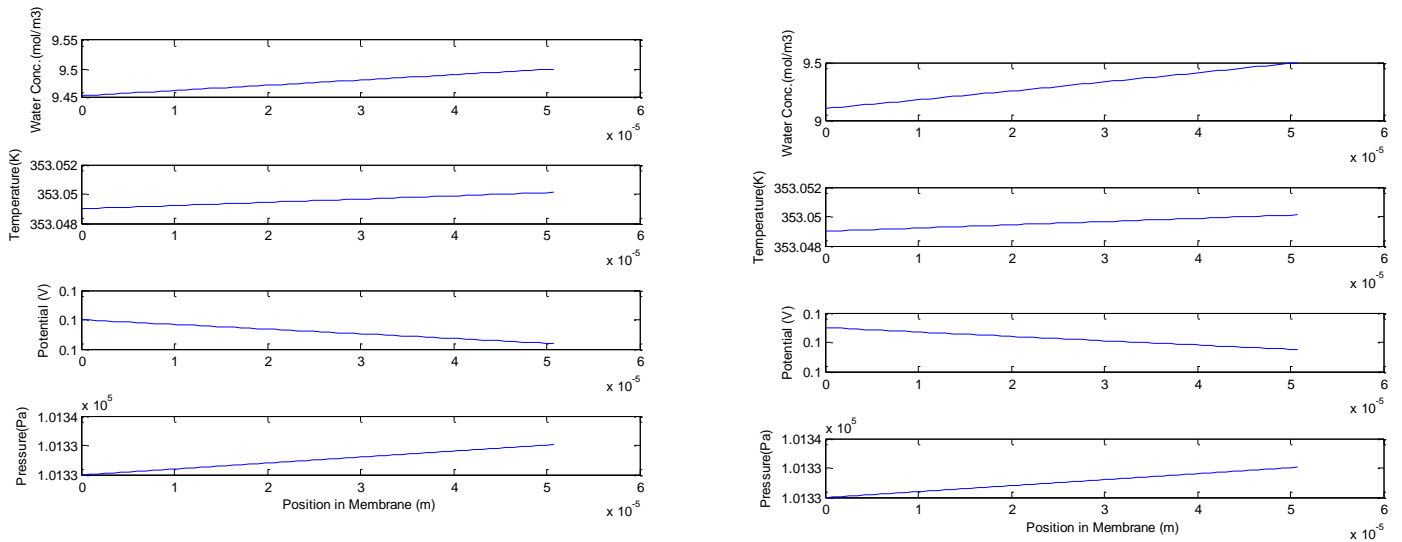
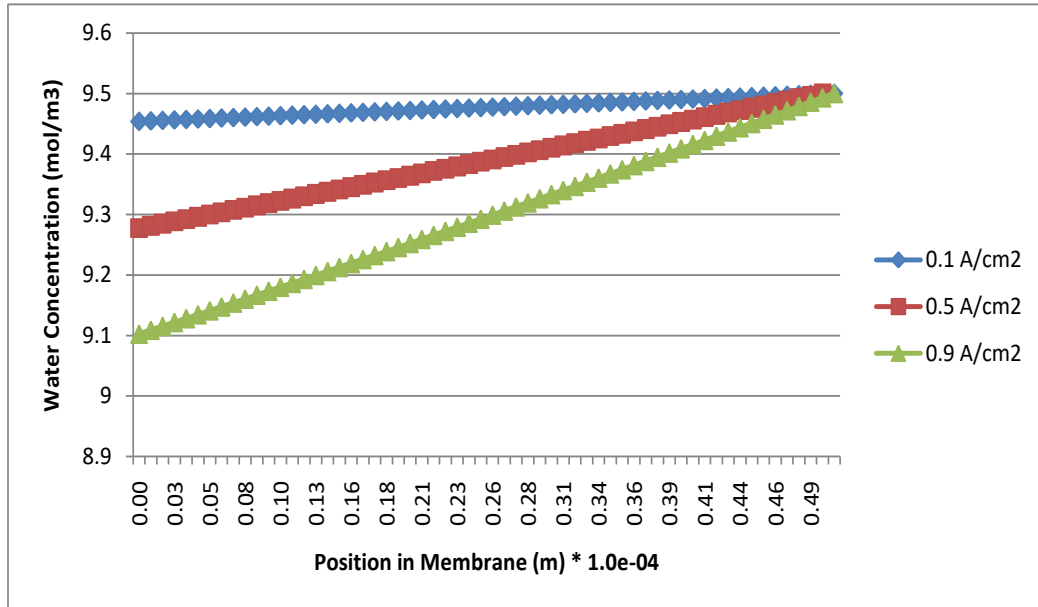


Figure. Water Concentration vs. Position in membrane for 8, 16 and 32 elements.

### 4.2 Effect of current density





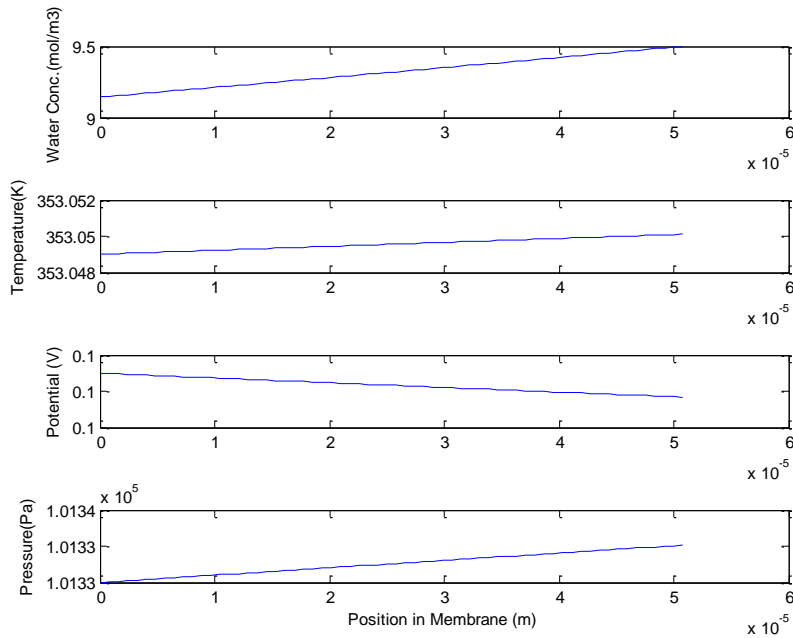


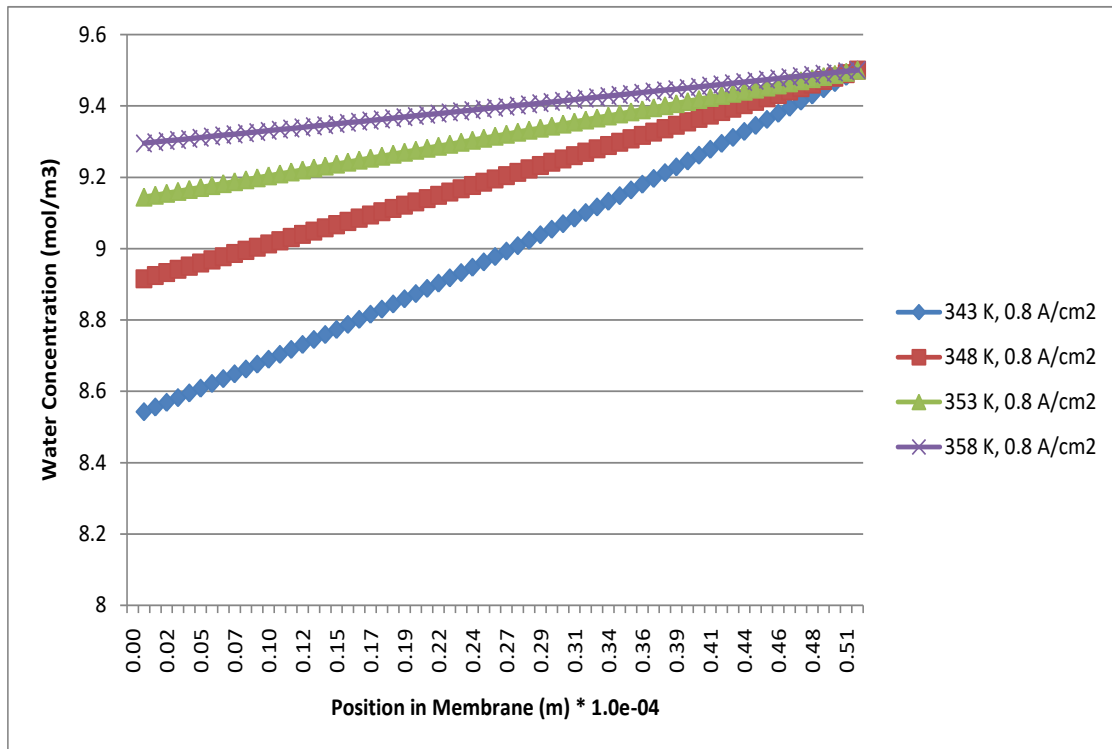
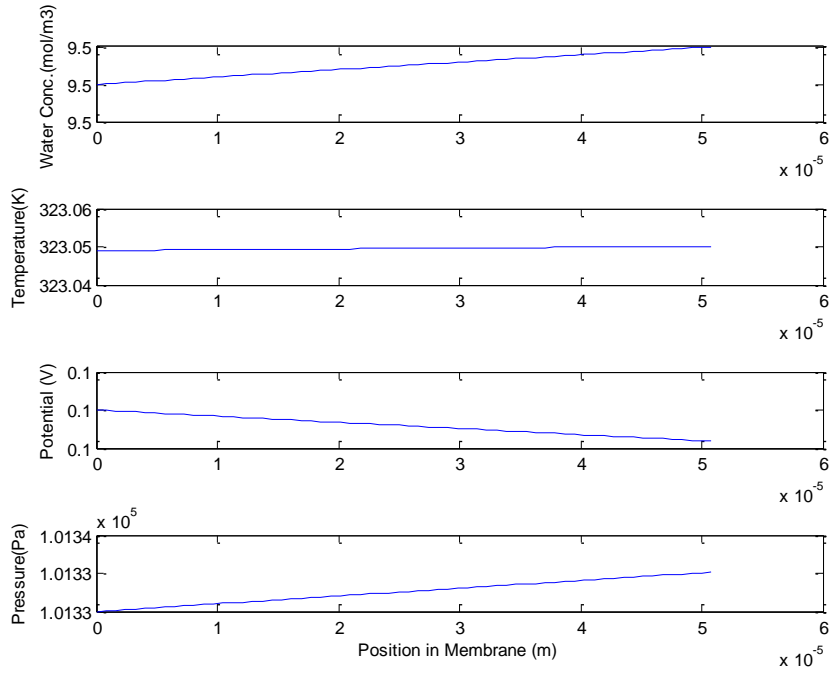
**Figure. Effect of current density on water concentration (a) 0.1 A/cm<sup>2</sup> (b) 0.9 A/cm<sup>2</sup> (c) comparison of 0.1 A/cm<sup>2</sup>, 0.5 A/cm<sup>2</sup> and 0.9 cm<sup>2</sup>.**

Figure. Demonstrates the effect of the electric drag force. As the current density increases, protons navigate from the anode where they are produced (left side of graph), to the cathode where they are consumed. As they migrate, the charged protons drag the dipole water concentration in the membrane changes through time with an applied current density. The solid lines show the water concentration with the specified applied current density. The water concentration on the anode side is lower with the higher applied current density. This is due to the increased number of water molecules on the cathode side. It is also true that the overall water content in the membrane is lower with higher current density. This is due to the increased protonic current dragging more molecules out of the membrane.

### 4.3 Effect of Temperature

Figure shows transient temperature profiles in the membrane when a small temperature gradient is established across the membrane. Under such conditions, the source term (ohmic heating) in the temperature conservation equation dominates. This results in a temperature increase across the membrane from the initial conditions established. Figure shows transient temperature profiles in the membrane when a much larger temperature gradient (20 C) is established across the membrane. In this case, convective effects begin to dominate. Although the source term is still present and supplying energy to the system, the convective effects dominate, and the temperature decreases across the membrane.





**Figure. Effect of temperature on water concentration (a) 353 K (b) 323 K (c) comparison of 343 K, 348 K, 353 K and 358 K.**

A clearer understanding of the membrane transport phenomena was obtained. A compact mathematical model using the `bvp` function in MATLAB was created that allows the user to specify the mesh size to analyze the conservation equations. The model developed is compact and can be a very powerful design tool for future investigations. The model solutions demonstrated many of the phenomena observed in proton exchange membranes and allowed a detailed analysis of the mass, heat and potential through the membrane. The higher the current density, the more water was driven from the anode to the cathode, and out of the membrane. A positive pressure gradient from the anode to the cathode could be used to drive water toward the anode side – which is more likely to dry out. The effect of the water flux into and out of the membrane illustrated that if too much water flows into the membrane, flooding may occur, whereas, if too much water is removed from the membrane, drying may occur. These results seem obvious, but the model allows these phenomena and their effect on temperature and voltage to be studied and quantified in detail. The model is also capable of predicting transient water, concentration voltage and temperature profiles for transient boundary conditions. This capability will prove useful when attempting to develop a control strategy for the fuel cell, and when investigating highly transient processes such as fuel cell startup on a vehicle.

## **5 Conclusion**

A simple model for water diffusion within Nafion membranes was created for both water concentration, temperature and potential.

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