

Transport Phenomena, Advanced Course,  
Fall semester 2018/19

Project 4-B: Membrane

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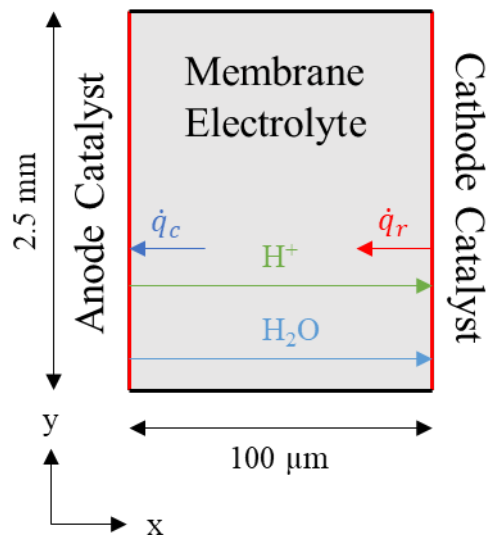
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# 1. Introduction

The aim of this project is to develop a numerical model of a proton exchange membrane fuel cell using *COMSOL*. A two-dimensional steady-state PEM model was constructed to study the concentration, velocity, and temperature profiles within the membrane. Figure 1 schematically shows a two-dimensional PEM. The model includes the transport of water and protons in the PEM that separates the anode and cathode catalysts. Hydrogen dissociates through oxidation at the anode catalyst into protons and electrons. The PEM is permeable to the diffusion of protons and water, but is an electrical insulator and does not conduct electrons. The electrons are conducted through an external circuit and supply power. Molecular oxygen is reduced at the cathode and oxygen ions combine with protons and electrons through a reduction reaction at the cathode side to form water.



**Figure 1.** Schematically shows the proton exchange membrane of a fuel cell. Protons and water flow through the membrane from the anode side and leave at the cathode side. Heat is generated from the internal resistance of the membrane towards charged carriers and at the cathode catalyst where the exothermic reaction of water formation takes place.

## 2. Theoretical Background

### 2.1. Governing Equations

The Molar flux of hydrogen ions was given as Eq. (1) and the molar flux of water is given as Eq. (2).

$$\dot{N}_{H^+} = -\frac{i}{F} \quad (1)$$

$$\dot{N}_{H_2O} = -\eta_{drag} \frac{i}{F} \quad (2)$$

Where  $i$  is the cell current density (A/m<sup>2</sup>),  $F$  is the *Faraday* constant (C/mol), and  $\eta_{drag}$  is the electro-osmotic coefficient representative of the potential of diffusing hydrogen to drag water molecules across the PEM. Half of the heat of reaction as shown in Eq. (3) from the exothermic electrochemical reaction of protons and oxygen ions at the cathode side reaches the membrane and the anode catalyst is kept at an operating temperature of 80 °C through convective cooling of water. Two protons are required to produce one molecule of water and half the heat of reaction is transferred to the membrane, which account for the 1/4 factor in the expression for the heat flux from the reaction.

$$\dot{q}_r = -\frac{\Delta H_r}{2} \frac{\dot{N}_{H^+}}{2} = -\frac{\Delta H_r}{4} \left( -\frac{i}{F} \right) \quad (3)$$

Due to internal resistance of the PEM towards charged carriers, such as protons, ohmic losses generate heat within the membrane according to Eq. (4).

$$\dot{q}_{loss} = -\frac{i}{\sigma_m} \quad (4)$$

Where  $\dot{q}_{loss}$  is the power loss per unit volume of the membrane (W/m<sup>3</sup>) and  $\sigma_m$  is the electrical conductivity of the membrane (S/m). The velocity distribution (convective mass transfer) within the porous proton exchange membrane is modelled after *Darcy's* law for laminar flow Eq. (5) and the conservation of mass expressed through the continuity equation Eq. (6).

$$u = -\frac{\kappa}{\mu} \nabla p \quad (5)$$

Where  $u$  (m/s) is the superstitial velocity distribution, which is related to the interstitial velocity by the porosity ( $\varepsilon$ ) of the membrane. The hydraulic membrane permeability is defined as  $\kappa$  (m<sup>2</sup>) and the fluid viscosity  $\mu$  in units of (Pa s). The negative sign accounts for the fluid flowing opposite the increasing pressure gradient  $\frac{\partial p}{\partial x}$  or pressure drop, flowing from a higher pressure to

a lower pressure. The pressure gradient vector  $\nabla p$  (Pa/m) describes the rate of pressure increase and its direction. The continuity equation Eq. (6) expresses the conservation of mass.

$$\nabla \cdot (\rho \mathbf{u}) = Q_m \quad (6)$$

$Q_m$  is a source term (kg/(m<sup>3</sup>s)) that accounts for the electrochemical reaction (the consumption of reactants and production of products). Assuming a constant density for incompressible fluids Eq. (6) reduces to Eq. (7).

$$\nabla \cdot (\mathbf{u}) = Q_m \quad (7)$$

The molar flux in a dilute electrolyte (PEM) has three contributions from diffusion, ionic migration, convection, and is expressed as Eq. (8). Diffusion is formulated after *Fick's* first law of diffusion, while the convective contribution is from *Darcy's* law Eq. (4). The contribution of the migration of ions is derived from the *Nernst-Einstein* relation, in which the electrochemical mobility is related to the diffusivity.

$$N_i = -D_i \nabla c_i - z_i u_i c_i \nabla \phi - c_i \mathbf{u} \quad (8)$$

Diffusion:	$-D_i \nabla c_i$
Ionic Migration:	$-z_i u_i c_i \nabla \phi$
Convective mass transfer:	$-c_i \mathbf{u}$

Where  $D_i$  is the diffusivity for each species (m<sup>2</sup>/s), in our case protons and water.  $c_i$  is the concentration of each species (mol/m<sup>3</sup>).  $z_i$  is the charge number of each species (dimensionless).  $\nabla \phi$  is the potential gradient (V/m).

Heat transfer is governed by the conservation of energy and for a porous medium is defined as Eq. (9).

$$(\rho C_p)_{eff} \frac{\partial T}{\partial t} + \rho C_p \mathbf{u} \cdot \nabla T + \nabla \cdot \mathbf{q} = Q \quad (9)$$

Where  $\rho$  is the fluid density (kg/m<sup>3</sup>),  $C_p$  is the fluid heat capacity at constant pressure (J/kg\*K),  $\mathbf{u}$  is the velocity field given by *Darcy's* law,  $\mathbf{q}$  is the conductive heat flux (W/m<sup>2</sup>) and expressed as *Fourier's* law of heat conduction Eq. (10).

$$\mathbf{q} = -k_{eff} \nabla T \quad (10)$$

Where  $\nabla T$  is the temperature gradient and  $k_{eff}$  the effective thermal conductivity of the porous membrane and is expressed as Eq. (11).

$$k_{eff} = \theta_p k_p + (1 - \theta_p)k \quad (11)$$

Where  $\theta_p$  is the volume fraction of solid material, which is equal to  $1 - \varepsilon$ . Furthermore,  $k$  is the thermal conductivity of water and  $k_p$  the thermal conductivity of the membrane.

## 2.2. Boundary Conditions

The boundary conditions implemented for a numerical solution of *Darcy's* law Eq. (4) were formulated by the pressure of 2.0 bar at the anode and 1.5 bar at the cathode sides, respectively. The governing molar flux equation Eq. (8) was implemented with the boundary conditions of the anode side flux equations of both  $\dot{N}_{H^+}$  and  $\dot{N}_{H_2O}$ , Eq. (1) and Eq. (2), respectively. The cathode side boundary condition has the depleted concentrations of protons ( $C_{H^+} = 0 \text{ mol/m}^3$ ) and a water concentration ( $C_{H_2O}$ ) dependent upon temperature. This is because the partial pressure of water should be at least three times the saturation pressure in order for the membrane to remain wetted, and the saturation temperature is dependent on the temperature of the water. The saturation pressure is given by the *Antoine* equation for pure water Eq. (12), and the concentration of water in the membrane is then calculated using the ideal gas law Eq. (13). The *Antoine* equation parameters from water from 0 to 100 °C and the pressure in units of mmHg is shown in table 1.

$$P = 10^{A - \frac{B}{C+T}} \quad (12)$$

Table 1: Parameters used for the *Antoine* equation.

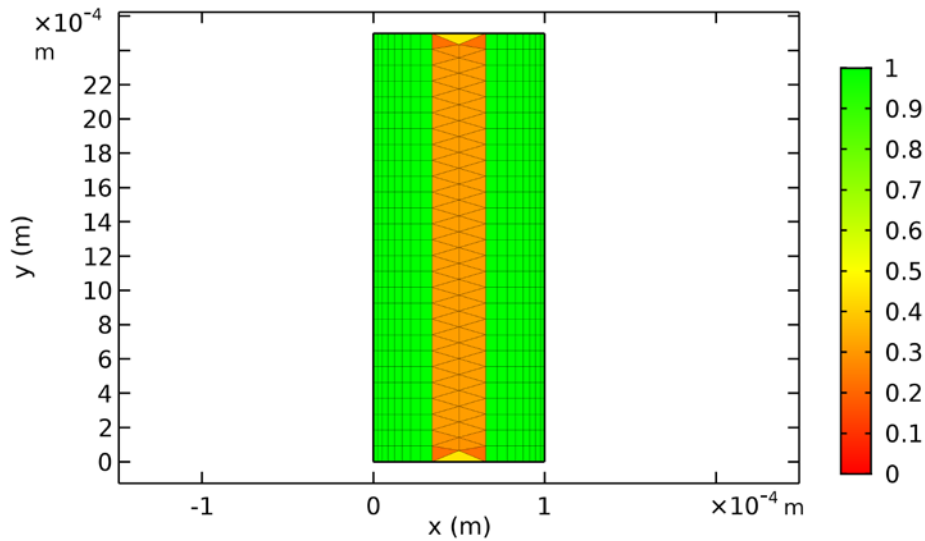
	A	B	C	T min. °C	T max. °C
Water	8.07131	1730.63	233.426	0	100

$$C_{H_2O} = 3C_{sat,H_2O} = \frac{P_{sat}}{RT} \quad (13)$$

Where  $R$  is the universal gas constant,  $T$  is the temperature in Kelvin, and the saturation pressure is determined from the *Antoine* equation, Eq (12). The boundary conditions for the governing heat transfer equation are a constant temperature of 80 °C at the anode catalyst and the heat transfer from the exothermic electrochemical reaction at the cathode side, which is half the heat of reaction that occurs at the cathode catalyst.

### 3. COMSOL Procedure

For the COMSOL model, the geometry of the membrane was modelled as a rectangle with the thickness in the x-direction and the height in the y-direction. The left boundary (at  $x = 0$ ) is the anode side and the one of the right is the cathode side (at  $x = 10^{-4} \text{ m}$ ). The top and bottom boundaries of the membrane are solid plate walls, with no mass or heat transfer across their boundaries. The grid mesh for this geometry consists of a boundary layer for the anode and the cathode side containing 8 layers with a stretching factor of 1.15 to account for the difference in height and thickness (aspect ratio) of the problem. In addition, the center of the membrane contains a predefined grid of finer element size. This was done in order to efficiently and accurately refine our model geometry mesh. The average skewness of the grid is 0.8619, as shown in figure 2, which accurately describes the boundaries. However, the center domain of the model is of less quality and accuracy due to relatively stretched elements. Nevertheless, the important part of the membrane are the boundaries where we expect larger fluctuations in the numerical solutions, so it is a good compromise.



**Figure 2.** Shows the applied grid for the model and the skewness is plotted as color bar.

Three physical models were implemented to account for the described equations: 1. “Darcy’s law”, 2. “Transport of Diluted species” and 3. “Heat Transfer of Porous Media”. The parameters used are listed in table 2. Further values for water were taken from the built-in library of *COM-SOL* and steady-state conditions were applied.

Table 2: Parameters for the *COMSOL* model

Description	Symbol	Value
Membrane height	$H$	2.5 mm
Membrane width	$W$	2.5 mm
Membrane thickness	$B$	100 $\mu\text{m}$
Membrane porosity	$\varepsilon$	0.4
Membrane density	$\rho_M$	1920 kg/m <sup>3</sup>
Membrane hydraulic permeability	$\kappa$	$8.9 \cdot 10^{-12}$ m <sup>2</sup>
Membrane thermal conductivity	$k_M$	0.95 W/(m·K)
Membrane specific heat capacity	$C_{P,M}$	1650 J/(kg·K)
Membrane Conductivity	$S$	7.5 S/m
Water specific heat capacity	$C_{P,H2O}$	2014 J/(kg·K)
Proton diffusion coefficient	$d_{H+}$	$4.5 \cdot 10^{-9}$ m <sup>2</sup> /s
electro-osmotic coefficient	$n_{drag}$	3
Catalyst operating temperature	$T_{cat}$	80 °C
Pressure on anode side	$p_{Anode}$	80 °C
Pressure on cathode side	$p_{Cathode}$	50 °C
Heat of electrochemical reaction	$\Delta H$	-273.3 kJ/mol
Cell current density	$i$	0.5 A/cm <sup>2</sup>
Cell potential	$E$	0.75 V
Fluid viscosity	$\mu$	$2.1 \cdot 10^{-5}$ Pa s

“Darcy’s law” is dependent on the pressure on both sides of the membrane, so that the pressure on the anode and cathode side were taken as boundary conditions. Furthermore, for the “Fluid and Matrix Properties” the porosity and the hydraulic permeability of the membrane, as well as the density and dynamic viscosity of water were added. The temperature was coupled to the “Heat Transfer of Porous Media”. Finally for the top and bottom boundary no flux was allowed.

The second module is dependent on the concentration of protons and water. They were implemented as boundary conditions at the cathode side, at which all protons are consumed for the water formation. The concentration of protons is therefore zero and to ensure that the membrane is always wet, the concentration of water is three times the saturation concentration obtained by the *Antoine* Law. As transport mechanisms “Convection”, “Migration in electric field” and “Mass transfer in a porous media” were allowed. For the “Transport Properties” the temperature was taken from “Heat Transfer of Porous Media” and the velocity field for convection from “Darcy’s law”. For diffusion the diffusion coefficients from water and protons were taken from the script and the membrane was assumed to be isentropic. The electric potential used for migration is 0 V at the anode side and -1 V at the cathode side. The mobility is obtained by the *Nernst-Einstein* relation and the charge of protons is set to +1 and for water to 0. The top and bottom boundaries were modeled as solid wall without any flux going through. As boundary condition



at the anode side, the inward flux of water and protons is related as described to the current density. Further by having steady-state conditions the molar flux needs to be constant at each point in x-direction.

Lastly, the third module “Heat Transfer of Porous Media” is dependent on the temperature and the thickness is set to the corresponding value from the table. As boundary condition the temperature at the anode side was kept constant at the catalyst temperature. The velocity field is obtained again by “*Darcy's* law. The fluid Material was set to water and all constants concerning the fluid were taken from the material library. For the membrane the volume fraction was set to  $1 - \varepsilon$  and the thermal conductivity, density and specific heat capacity were taken from the script and can be found in table 2. The upper and lower boundaries were modelled as thermal insulating walls. The heat generation by the Ohmic resistance of the membrane was modelled as heat source with the expression from Eq. (4). The heat from the reaction was modeled as heat flux from the cathode side with the expression from Eq (3).

For the solver a relative tolerance of 0.001 was used.

## 4. Results and Discussion

From the *COMSOL* model profiles concerning velocity, temperature and concentration across the membrane were obtained. The velocity enters the model by *Darcy's* law, therefore a constant velocity profile due to the linear pressure drop should be expected, in contrast to figure 3.

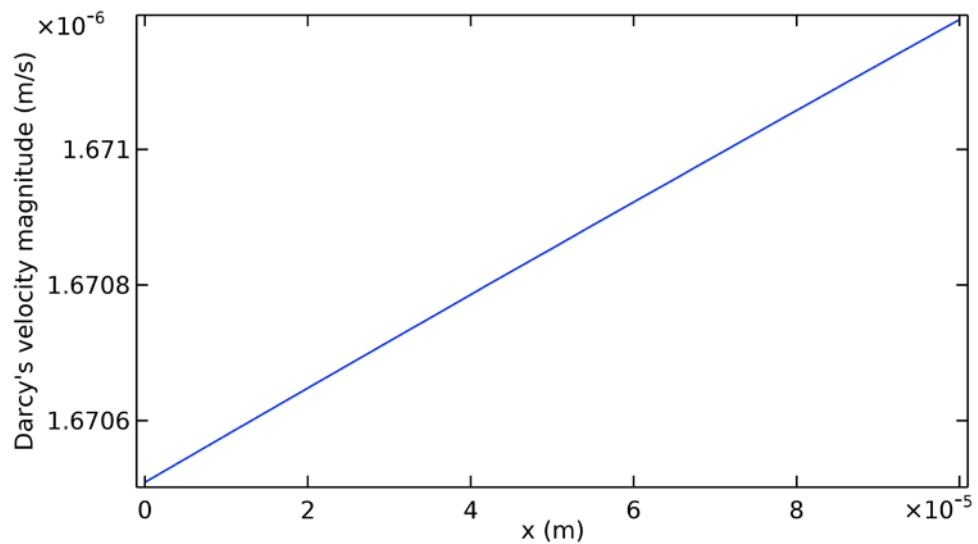


Figure 3. Shows the velocity profile obtained by *Darcy's* law across the membrane.

The slight increase in the velocity profile is due to the change of the dynamic viscosity of water, which is dependent on the temperature. At higher temperature the viscosity decreases and therefore the velocity by *Darcy* increases slightly. A comparison with the temperature profile depicted in figure 4, validates this.

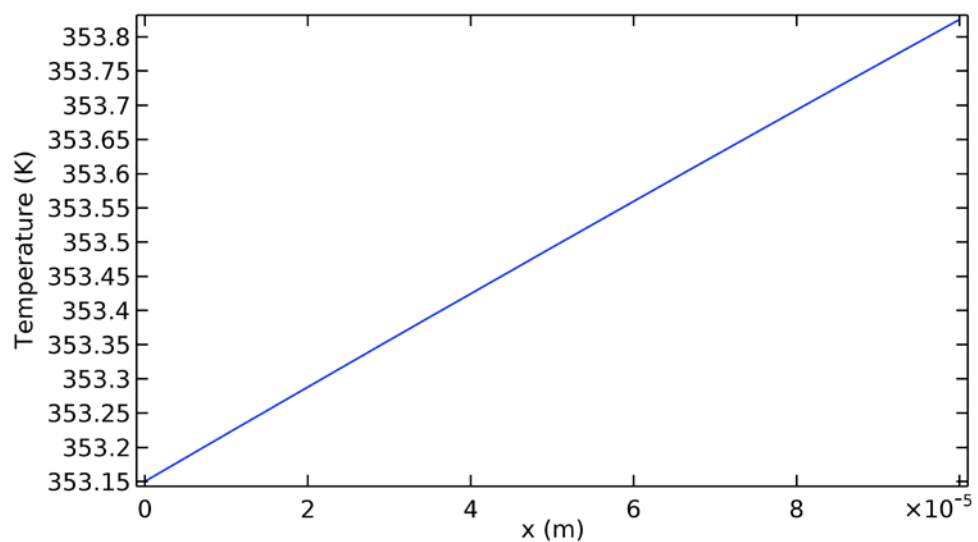
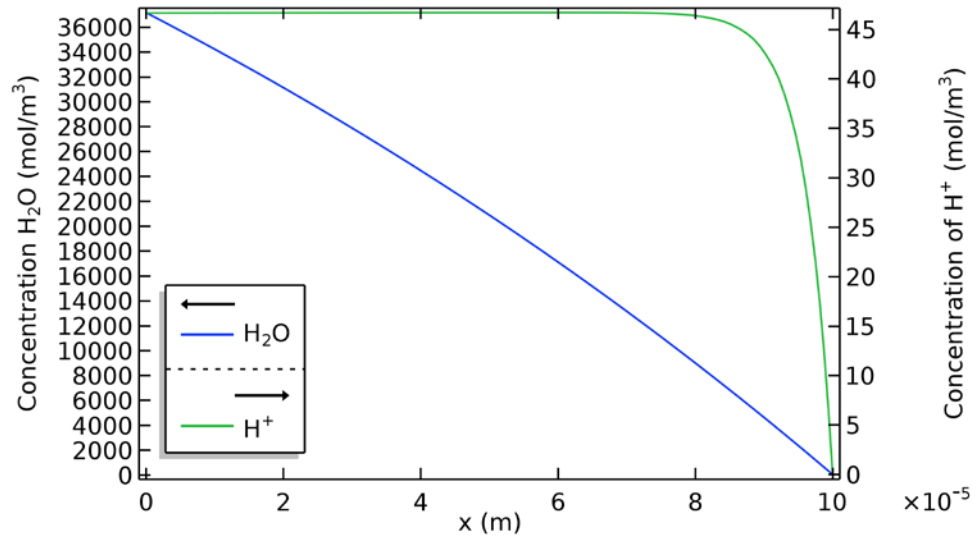


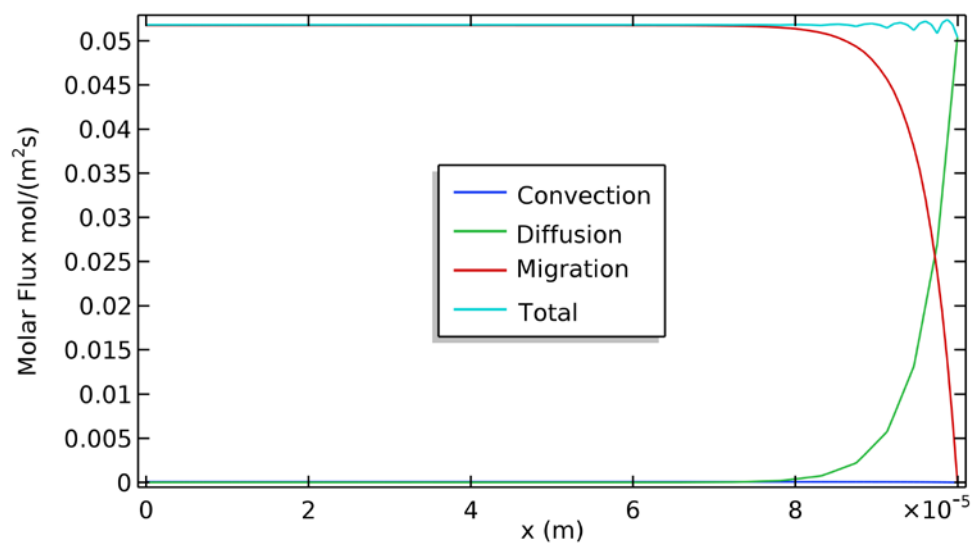
Figure 4. Shows the temperature profile across the membrane.

As explained there is a slight increase in temperature through the membrane by the reaction at the cathode and the heat generated from the resistance in the membrane. For the general mass balance equation migration, convection and diffusion need to be considered in case of protons and only diffusion and convection for the water. The corresponding profiles are shown in figure 5.



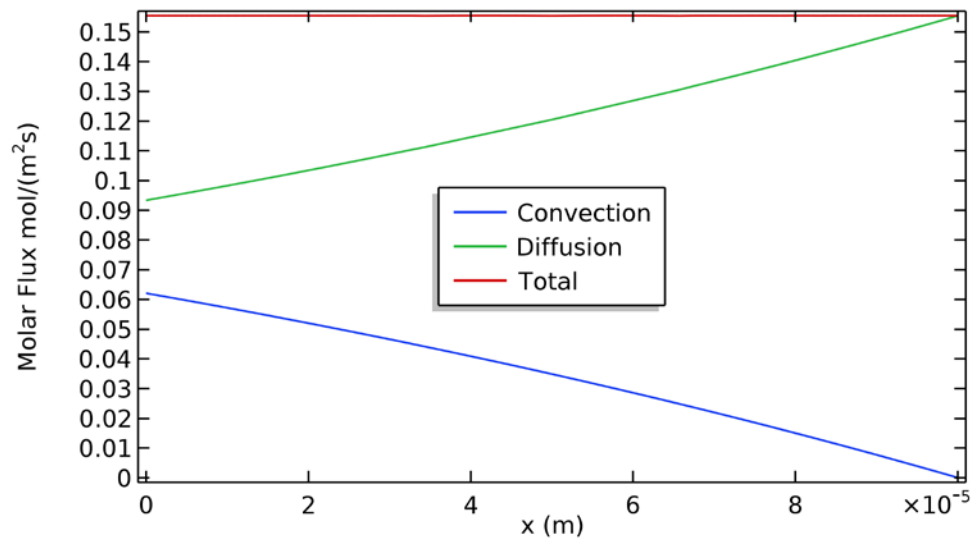
**Figure 5.** Shows the concentration profiles of protons and water across the membrane.

The concentration profile differs a lot, so that the concentration of protons is almost constant until 80% of the membrane and then it drops rapidly. On the other hand water is decreasing linearly with a slight curvature in it. The difference can be better seen by the molar fluxes as for protons shown in figure 6.



**Figure 6.** Shows profile of the molar flux of protons concerning the different transport mechanisms.

The constant concentration at the beginning is due to migration and the molar flux from migration drops rapidly when approaching the cathode side. The molar flux of diffusion increases by the same amount migration is decreasing. Therefore for the protons migration is governing the concentration, except for the right boundary where diffusion becomes important as well. Migration is dependent on the concentration and therefore the concentration profile is a constant at the beginning, but diffusion is dependent on its gradient therefore it drops dramatically at the border to fulfill the boundary condition. The non-constant total molar flux of protons is an artifact from solving the problem numerically and refining the grid or changing the relative tolerance does not affect it. Another thing to notice is the vanishing impact of convection, so that it could be neglected for the protons. Water, which is not affected, by migration behaves different as shown in figure 7.



**Figure 7.** Shows profile of the molar flux of water concerning the different transport mechanisms.

Diffusion and convection are of similar magnitude for water. For a membrane without convection a linear concentration profile would be assumed, because the total molar flux needs to be constant. By including convection diffusion is varying in x-direction, so that we have a curved concentration profile as stated before, the concentration gradient is increasing in x-direction. Therefore for water the convection is not negligible and needs to be included, in contrast to the protons. The total molar flux stays constant for water, so that problems arise by including the third mechanism, therefore it might improve by assuming no convection for protons.

## 5. Conclusions

The developed model is capable of describing a membrane in a steady-state including three mass transport mechanism and two sources of heat. It is therefore more sophisticated than the membrane models presented in the lecture. Nevertheless by including three terms for the mass transport noise reducing slightly the accuracy was introduced. An improvement might be to reduce the number of transport mechanisms that would be suitable for protons because mass transport is mainly governed by migration and diffusion. The simple model is capable of describing a stationary membrane in a fuel cell, but in most applications, e.g. automobiles, this is a rather bad assumption. To model this time-dependent solutions would be necessary, which are computationally much more demanding. Furthermore, a fuel cell does only work, if all parts of a cell are combined (the whole is greater than the sum of its parts), so more components need to be added to this model to capture electrochemical phenomena.