Unsteady state model of water content inside membrane of Polymer Electrolyte Membrane Fuel cell

Sasi Kiran

A Thesis Submitted to
Indian Institute of Technology Hyderabad
In Partial Fulfillment of the Requirements for
The Degree of Master of Technology

भारतीय प्रौद्योगिकी संस्थान हैदराबाद
Indian Institute of Technology Hyderabad

Department of Chemical Engineering

June, 2014

Declaration

I declare that this written submission represents my ideas in my own words, and where others' ideas or words have been included, I have adequately cited and referenced the original sources. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/data/fact/source in my submission. I understand that any violation of the above will be a cause for disciplinary action by the Institute and can also evoke penal action from the sources that have thus not been properly cited, or from whom proper permission has not been taken when needed.

_____Shashi Kiran_
(Signature)

_____Seelam Sasi Kiran
(Sasi Kiran)

__CH12M1015_

Approval Sheet

This thesis entitled **Unsteady state model of water content inside membrane of PEMFC** by Seelam Sasi Kiran is approved for the degree of Master of Technology from IIT Hyderabad.

(Dr. Vinod Janardhanan) HOD
Department of Chemical Engineering
IITH

(Dr. Phanindra Jampana) Guide
Department of Chemical Engineering
IITH

(Dr. Parag D Pawar) Examiner
Department of Chemical Engineering
IITH

(Ketan P. Detroja)External Examiner
Department of Electrical Engineering
IITH

Acknowledgements

First and foremost , I would like to express my sincere gratitude to my Guide Dr. Phanindra Varma Jampana and Co-Guide Dr. Dayadeep Monder for their invaluable support and patience in completion of my thesis.

I am also grateful to the Department of Chemical Engineering , IIT Hyderabad who supported me during the hard times .

Dedicated to

My Family

Abstract

Polymer Electrolyte Membrane Fuel cell (PEMFC) having highest power density compared to other fuel cells . Operation temperature < 100ºC mainly considered for portable applications . Its uses are endless starting from space shuttle to Fuel cell cars in Automobile Industry . I have derived necessary equations for unsteady state PEMFC model and then I used COMSOL for modelling to analyze how water content inside PEMFC would change with respect to space coordinate and time based on the inlet conditions .

Contents

List of Figures

List of Tables

Nomenclature

1	Anode interface
2	anode electrode to membrane interface
3	Membrane to cathode interface
4	Cathode to cathode plenum interface
A	anode region
B	component B
C	cathode region
H	Hydrogen
N	Nitrogen
O	oxygen
Mem	Membrane
Sat	saturation
W	water
I	Initial value entering inlet flow channels
L	Final value leaving inlet flow channels
D	diffusion coefficient cm^2/s
F	faraday constant 96484 C/mol
I	water molar flux produced at cathode
J	current density A/cm^2

M_m	Equivalent weight of membrane
M_w	Molecular weight of water (kg/mole)
$Ŋ_{drag}$	Electro-osmotic drag coefficient
N_{wA}	anode water flow rates or flux
$N_{H2,1}$	Hydrogen flux at interface 1
$N_{O2,4}$	Oxygen flux at interface 4
N_O^I	Inlet Oxygen flux
N_N^I	Inlet nitrogen flux
N_{wC}	Cathode water flux
N_{Wc}^I	Cathode water flux at inlet
N_{Wc}^L	Cathode water flux leaving
N_{total} ,c^L	Total cathode flux leaving
N	Molarflux, mol/cm^2 s
p_c	critical pressure , atm
P	pressure,atm
R	molar gas constant (J/K* mole)
R_{cell}	membrane resistance Ω cm^2
t	thickness, cm
T	temperature ,^{0}C
T_c	critical temperature ,K
V	cell potential V
x	mole fraction

X_{WA}^{I}	mole fraction of water at anode inlet
X_{WC}^{I}	mole fraction of water at cathode inlet
X_{O}^{I}	mole fraction of oxygen at inlet
X_{ON}	Inlet dry gas mole fraction of oxygen
X_{O4}	Oxygen molefraction at interface 4
X_{w4}	Water molefraction at interface 4
X_{W1}	Mole fraction of water at interface 1
P_{A}	pressure at anode (atm)
P_{A}^{SAT}	saturation pressure at anode(atm)
P_{C}^{SAT}	saturation pressure at cathode(atm)
P_{C}	pressure at cathode(atm)
Z	distance variable (cm)
α	ratio of net H_2O flux in membrane to H_2O flux product at cathode
β	ratio ofnet H_2O flux in membrane to H^- flux in membrane
λ	water content or local ratio H_2O/SO_3^- in the membrane
ρ	density (g/cm^3)
ν	stoichiometric coefficient
ν_H	stoichiometric coefficient ratio of hydrogen $\nu_{H} = N_{H2}^{I} / N_{H2,1}$
ν_o	stoichiometric coefficient ratio of hydrogen $\nu_{o} = N_{o}^{I} / N_{o,1}$
D_{wH}	Diffusivity coefficient between water and hydrogen
D_{wO}	Diffusivity coefficient between water and oxygen (m^2/s)
D_{ON}	Diffusivity coefficient between nitrogen and oxygen(m^2/s)

Dw_N	Diffusivity coefficient between nitrogen and water(m^2/s)
a	water vapor activity
c_w	water concentration
e_a	Mass coefficient
d_a	Damping or Mass coefficient
Γ	Conservative Flux
f	Source Term
A	Area of cell
I	Molar flux
J	Cell current $\left({}^{A}/_{cm^2}\right)$
n_d	Number of water molecules per proton
D_λ	Diffusion constant$\left({}^{cm^2}/_{s}\right)$
M_m	Equivalent molecular weight of membrane $\left({}^{g}/_{mol}\right)$
x_w	Mole fraction of water
P	Total pressure (atm)
P_{sat}	saturated pressure of water (atm)
ρ	density of dry membrane (kg/m^3)
a	water vapour activity
N	No cells used in fuel cell
A_a	Active area of anode (cm^2)
i	current density (amp/cm^2)
t_a	Thickness of anode (cm)
t_c	Thickness of cathode (cm)
F	Farady const (coulomb/mole)

Chapter 1 : Introduction

1.1 Fuel cells

A fuel cell is a device which converts chemical energy of fuel in to electrical energy (DC electricity) through electro chemical reactions . Heat and water are it's by products .

The first fuel cell was demonstrated by Sir William Robert Grove in 1839 .

Types of Fuel cell

There are five major types of fuel cells

1. Phosphoric acid fuel cell (PAFC)
2. Polymer electrolyte membrane fuel cell (PEMFC)
3. Alkaline fuel cell (AFC)
4. Molten carbonate fuel cell (MCFC)
5. Solid oxide fuel cell (SOFC)

Every Fuel cell has their own advantages , This Thesis is restricted to PEMFC (Polymer electrolyte membrane fuel cell).

1.2 Polymer Electrolyte Membrane Fuel Cell

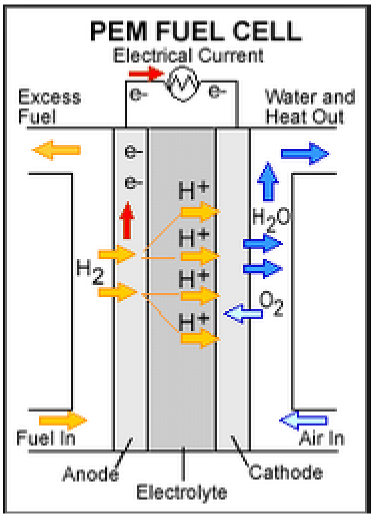

Figure 1.2 : Schematic diagram of PEMFC

In the above figure which shows that humidified saturated Hydrogen gas is passed through anode and humidified saturated oxygen gas(in the form of air) is passed through cathode , after electrochemical reactions occurring at anode-membrane interface and cathode-membrane interface water is produced at cathode , while electrons move through external circuit . The half reactions at anode and cathode are given below [3].

Half reaction at Anode:

$$H_2 \rightarrow 2H^+ + 2e^- \tag{1.2}$$

Half reaction at Cathode:

$$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \tag{1.3}$$

Total reaction

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \tag{1.4}$$

1.2.1 Anode

In PEMFC where anode is made of platinum [7] , Humidified saturated Hydrogen is passed as inlet gas for anode which converts Hydrogen gas to H^+ ions and e^- , which passes through membrane to the cathode side and electrons moves through the external circuit as given in the figure .

Half reaction at Anode:

$$H_2 \rightarrow 2H^+ + 2e^-$$

1.2.2 Cathode

In PEMFC where cathode is made of platinum , oxygen gas as inlet for cathode side the H^+ and the e^- moving from the anode side reacts with oxygen gas and leads to the formation of water at cathode , as seen in the figure .

Half reaction at Cathode:

$$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$$

1.2.3 Membrane

Nafion is used as a membrane in PEMFC , which is porous in structure its thickness is in the range of 20-200 microns . Membrane is coated with platinum on either side of it along with support material , here it is carbon (support material) . PEMFC works at < 100°C(celcius) , most of the experimental data obtained in PEMFC would be at 70-80°C(celcius) for this low operating temperature platinum is used as feasible catalyst .

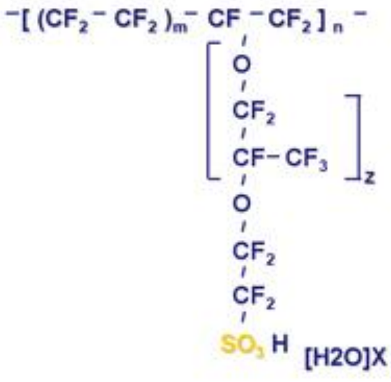

Fig 1.2.3: Nafion structure[3]

1.2.4 Membrane electrode assembly

MEA (Membrane electrode assembly) is a combination of anode ,membrane and cathode in a sandwich form with a thickness of 1mm [6] . Since the power generated is used for portable applications (<1KW) , Hydrogen is used as anode for such applications . Methanol and formic acid can also be considered as fuel for PEMFC process . The power density obtained using PEMFC is more compared to all other fuel cells around 300-1000 mW/cm^2 . Automobile Industry started launching their cars using PEMFC concept since 2009 , Some of the notable releases are Honda FCX clarity , GM HydroGen4 , Mercedes-Benz F-Cell.

1.2.5 PEMFC Advantages and Disadvantages

PEMFC advantages

1. PEMFC has the highest power density [3] compared to other fuel cells
2. Since it has very good start and stop abilities , Automobile sector is been dominated by PEMFC concept cars.
3. The operating temperature is < 100ºC and power generated is < 1KW , so it can be used for portable uses .

PEMFC disadvantages

1. In PEMFC platinum is used as catalyst and it’s very expensive.
2. The membrane used in PEMFC is sensitive and costly.
3. Relative humidity need to be taken care of PEMFC otherwise it leads to drying of membrane.
4. Flooding in fuel cell arises if proper water management is not used in PEMFC.

1.3 Scope and Plan of thesis

This work mainly focus on the time dependent model of PEMFC using COMSOL , Firstly in order to understand time dependent model , I have simulated time independent model that is mole fraction of species at anode and cathode with respect to space using Springer et al [1] model equations , then I have derived time dependent equations and simulated results .

Chapter 2 : Modelling

2.1 Steady state model of PEMFC

To understand the membrane mechanism , one dimensional steady state model is considered.

The accumulation of more water in the cathode is called flooding and decrease in the free volumes of membrane is called drying , which are major concerns of PEMFC . In flooding the back diffusion of water takes place in the cell. This thesis uses polymer electrolyte fuel cell model by T.E springer , T.A Zawodzinski and S.Gottesfeld [1] for the development of equations.

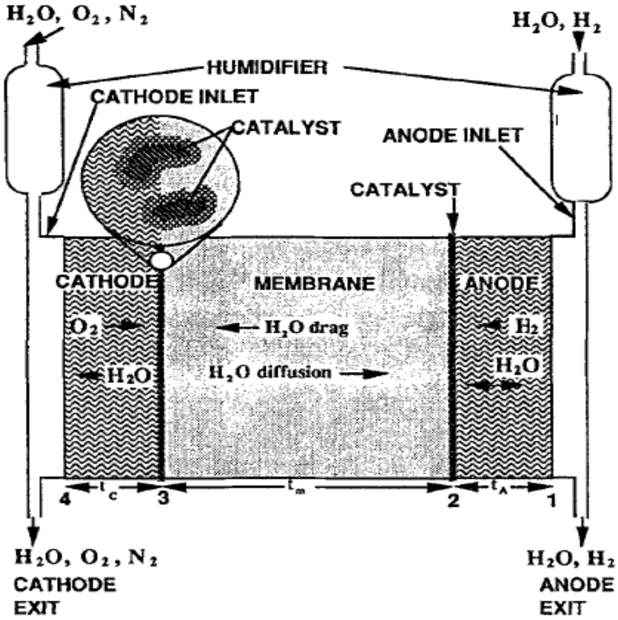

Figure 2 : Schematic diagram of PEMFC [1]

Assumptions

1. The cell is considered to be isothermal between the inlet channels .
2. Entrained droplets as transport mechanism for water .

3. Under steady state N_2 flow is always be zero.
4. Fluid composition in the anode and cathode flow channels is assumed to be uniform.
5. Anode and cathode gas mixtures with water vapor act as ideal gas .
6. The model considers only concentration gradients , not total pressure gradients across the electrodes

The governing equations for solving 1-D model with respect to space are as follows

Water balance along anode is given by below equation

$$\frac{dx_{WA}}{dz} = \frac{RTI(\, x_{WA}\,(1+\alpha)-\alpha)}{P_A D_{WH}} \tag{2.1}$$

Pressure diffusivity is calculated at critical temperature and critical pressure they are given by

$$P.D_{AB} = a\left(\frac{T}{\sqrt{T_{cA}T_{cB}}}\right)^{b} (P_{cA}P_{cB})^{1/3}(T_{cA}T_{cB})^{5/12}\left(\frac{1}{M_A}+\frac{1}{M_B}\right)^{1/2} \varepsilon^{3/2} \tag{2.2}$$

$a = 0.0002745$

$b = 1.832$ for hydrogen , oxygen and nitrogen $\varepsilon^{3/2}$ = correction factor

Oxygen balance along cathode is given by following equation

$$\frac{dx_o}{dz'} = \frac{RTI}{P_C}\left[\frac{x_O(1+\alpha)+(0.5x_{wc})}{D_{wO}} + \frac{1-x_{wC}-x_O}{D_{OW}}\right] \tag{2.3}$$

Relation between Swollen membrane in terms of dry membrane given as follows

$$Z' = (1+S\lambda)Z \tag{2.4}$$

λ = water content inside membrane

mole fraction of water along cathode is given

$$\frac{dx_{WC}}{dz'} = \frac{-RTI}{P_C}\left[\frac{(1-x_{WC}-x_O)(1+\alpha)}{D_{WN}} + \frac{0.5x_{WC}+x_O(1+\alpha)}{D_{ON}}\right] \tag{2.5}$$

these two simultaneous equations are solved to get profile for mole fraction of water and oxygen along cathode length.

The diffusion of water vapor is given by following equation in terms of membrane properties.

$$N_{w,dif} = -D'c_w \frac{d\,(\ln a)}{d\lambda}\frac{d\lambda}{dz'} = -D'\left(\frac{\lambda^{\rho_{dry}}/_{M_m}\left(\frac{\lambda}{a}\right)\left(\frac{da}{d\lambda}\right)}{(1+s\lambda)^2}\right)\frac{d\lambda}{dz} = -\left(\frac{\rho_{dry}}{M_m}\right)\left(\frac{d\lambda}{dz}\right)D_\lambda$$

2.2 Unsteady state model of PEMFC

2.2.1 Unsteady state equation for water content inside membrane

Rate of accumulation = Rate in – Rate out + Rate of generation – Rate of consumption

$$\frac{\partial c_w}{\partial t} + \nabla . j = \sigma \qquad (2.2.1)$$

j_1= diffusion

j_2= N_{drag}

$$j = j_1 + j_2 \qquad (2.2.2)$$

$$\nabla j_1 = \left(\frac{\partial i}{\partial x} + \frac{\partial j}{\partial y} + \frac{\partial k}{\partial z}\right)\left(\frac{\partial \mu}{\partial z'}\right)\left(-\frac{D' c_w}{RT}\right)k \qquad (2.2.3)$$

$$\nabla j_1 = \left(-\frac{D' c_w}{RT}\frac{\partial}{\partial z}\left(\frac{\partial \mu}{\partial z'}\right)\right) \qquad (2.2.4)$$

$$N_{drag} = \frac{5\lambda I}{22} \qquad (2.2.5)$$

$$\nabla j_2 = \left(\frac{\partial i}{\partial x} + \frac{\partial j}{\partial y} + \frac{\partial k}{\partial z}\right) * (N_{drag} * (-k)) \qquad (2.2.6)$$

$$\nabla j_2 = \left(-\frac{\partial N_{drag}}{\partial z}\right) \qquad (2.2.7)$$

Relation between Swollen membrane in terms of dry membrane given as follows

$$Z' = (1 + S\lambda)Z \tag{2.2.8}$$

λ = water content inside membrane

Applying limit to the above equation we get

$$c_w = \frac{\rho * \lambda}{M_m * (1 + s\lambda)} \tag{2.2.9}$$

$$\frac{\rho}{M_m} * \frac{\partial}{\partial t}(\frac{\lambda}{1 + s\lambda}) = -2I\ \frac{\partial n_d}{\partial Z} - \frac{\rho}{M_m}\frac{\partial}{\partial Z}\left(D_\lambda * \frac{\partial \lambda}{\partial Z}\right)$$

$$\frac{\rho}{M_m} * \frac{\partial}{\partial t}\left(\frac{\lambda}{1 + s\lambda}\right)$$
$$= -2I\ \frac{\partial}{\partial Z}\left(2.5 * \frac{\lambda}{22}\right) - \frac{\rho}{M_m}$$
$$* \frac{\partial}{\partial Z}\left(\frac{1}{(1 + s\lambda)^2} * \frac{\lambda}{a(17.81 - 79.79a + 108 * a^2)}\right) D'\ \frac{\partial \lambda}{\partial Z}$$

$$\frac{\rho}{M_m * (1 + s\lambda)^2} * \frac{\partial \lambda}{\partial t}$$
$$= \left(\frac{-5I}{22} * \frac{\partial \lambda}{\partial Z}\right) - \frac{\rho}{M_m} * \frac{D'}{a(17.81 - 79.79a + 108 * a^2)} * \frac{\partial}{\partial Z}\left(\frac{\lambda}{(1 + s\lambda)^2} * \frac{\partial \lambda}{\partial Z}\right)$$

$$\frac{\rho}{M_m} * \frac{\partial \lambda}{\partial t}$$
$$= \left(\frac{-5I}{22} * \frac{\partial \lambda}{\partial Z}\right) - \frac{\rho}{M_m} * \frac{D'}{a(17.81 - 79.79a + 108 * a^2)} * \frac{\partial}{\partial Z}\left(\frac{\lambda}{(1 + s\lambda)^2} * \frac{\partial \lambda}{\partial Z}\right)$$

$$a = \frac{x_w * P}{P_{sat}} \tag{2.2.11}$$

UNSTEADY STATE BALANCE EQUATIONS AT CATHODE AND ANODE

Continuity equations [2] for species α can be written as

$$c\left(\frac{\partial x_\alpha}{\partial t} + (v^*.\nabla x_\alpha)\right) = -(\nabla.J_\alpha^*) + R_\alpha - x_\alpha \sum_{\beta=1}^{N} R_\beta \tag{2.2.12}$$

Where α=1,2,…N

Rate of increase in moles of A per unit volume + Net rate of addition in moles of A per unit volume by convection = Rate of addition of moles of A per unit volume by diffusion + Rate of production of moles of A per unit volume by reaction – Rate of consumption of moles of A per unit volume by reaction

$$v^* = \sum_{\alpha=1}^{N} x_\alpha v_\alpha \tag{2.2.13}$$

v^*= molar average velocity

$$J_\alpha^* = -c\, D_{AB} \nabla x_\alpha \tag{2.2.14}$$

$$c_\alpha = c * x_\alpha \tag{2.2.15}$$

At anode humidified hydrogen is been sent as inlet

So the modified equation is given by [2]

$$\frac{c_\alpha}{x_\alpha}\left(\frac{\partial x_\alpha}{\partial t} + (v^*.\nabla x_\alpha)\right) = \frac{c_\alpha}{x_\alpha} D_{AB}\, \nabla^2 x_\alpha + R_\alpha - x_\alpha \sum_{\beta=1}^{N} R_\beta \tag{2.2.16}$$

For Anode H_2 , H_2O are species

$$\frac{c_{H_2}}{x_{H_2}}\left(\frac{\partial x_{H_2}}{\partial t} + \left(v^*.\frac{\partial x_{H_2}}{\partial Z}\right)\right) = \frac{c_{H_2}}{x_{H_2}} D_{AB} \frac{\partial^2 x_{H_2}}{\partial Z} + R_{H_2} - x_{H_2}(R_{H_2} + \cancel{R_{H_2O}}) \tag{2.2.17}$$

R_{H_2} = H_2 reacted during reaction

v^*= molar average velocity

R_{H_2O}=H_2O produced at cathode

For $D_{AB}\, \nabla^2 x_\alpha$ Maxwell steffan equation[11] approach for binary diffusion given by

$$\begin{bmatrix} 1 & D_{H_2-H_2O} \\ D_{H_2-H_2O} & 1 \end{bmatrix} \begin{bmatrix} \nabla^2 x_{H_2} \\ \nabla^2 x_{H_2O} \end{bmatrix} \tag{2.2.18}$$

$$\frac{c_{H_2O}}{x_{H_2O}}\left(\frac{\partial x_{H_2O}}{\partial t} + \left(v^*.\frac{\partial x_{H_2O}}{\partial Z}\right)\right) = \frac{c_{H_2O}}{x_{H_2O}} D_{AB} \frac{\partial^2 x_{H_2O}}{\partial Z} + R_{H_2O} - x_{H_2O}(R_{H_2} + \cancel{R_{H_2O}}) \tag{2.2.19}$$

R_{H_2O} is not considered because there is no production of water at anode side

For cathode H_2O , N_2 , O_2 are the species

$$\frac{c_{H_2o}}{x_{H_2o}}\left(\frac{\partial x_{H_2o}}{\partial t}+\left(v^{*}.\frac{\partial x_{H_2o}}{\partial Z}\right)\right)$$
$$=\frac{c_{H_2o}}{x_{H_2o}}D_{CD}\,\frac{\partial^2 x_{H_2o}}{\partial Z}+R_{H_2o}-x_{H_2o}(R_{O_2}+R_{H_2O}+\cancel{R}_{N_2})$$

(2.2.20)

R_{N_2} is neglected because N_2 is not participating in the reaction

$D_{CD}\,\nabla^2 x_\alpha$, maxwell steffan [11] approach for multicomponent diffusion approach given by

$$\begin{bmatrix} 1 & D_{O_2-H_20} & D_{O_2-N_2} \\ D_{O_2-H_20} & 1 & D_{H_20-N_2} \\ D_{O_2-N_2} & D_{H_20-N_2} & 1 \end{bmatrix}\begin{bmatrix} \nabla^2 x_{o_2} \\ \nabla^2 x_{H_2o} \\ \nabla^2 x_{N_2} \end{bmatrix}$$

(2.2.21)

$$\frac{c_{o_2}}{x_{o_2}}\left(\frac{\partial x_{o_2}}{\partial t}+\left(v^{*}.\frac{\partial x_{o_2}}{\partial Z}\right)\right)=\frac{c_{o_2}}{x_{o_2}}D_{CD}\,\frac{\partial^2 x_{o_2}}{\partial Z}+R_{o_2}-x_{o_2}(R_{O_2}+R_{H_2O}+\cancel{R}_{N_2})$$

(2.2.22)

$$R_{H_2}=\frac{N*A_a*i}{A_a*\ t_a*2F}$$

(2.2.23)

$$R_{H_2}=-\frac{N*i}{t_a*2F}$$

(2.2.24)

$$R_{H_2o}=\frac{N*i}{t_c*2F}$$

(2.2.25)

$$R_{o_2}=-\frac{N*i}{t_c*4F}$$

Chapter 3: Modelling of PEMFC in COMSOl

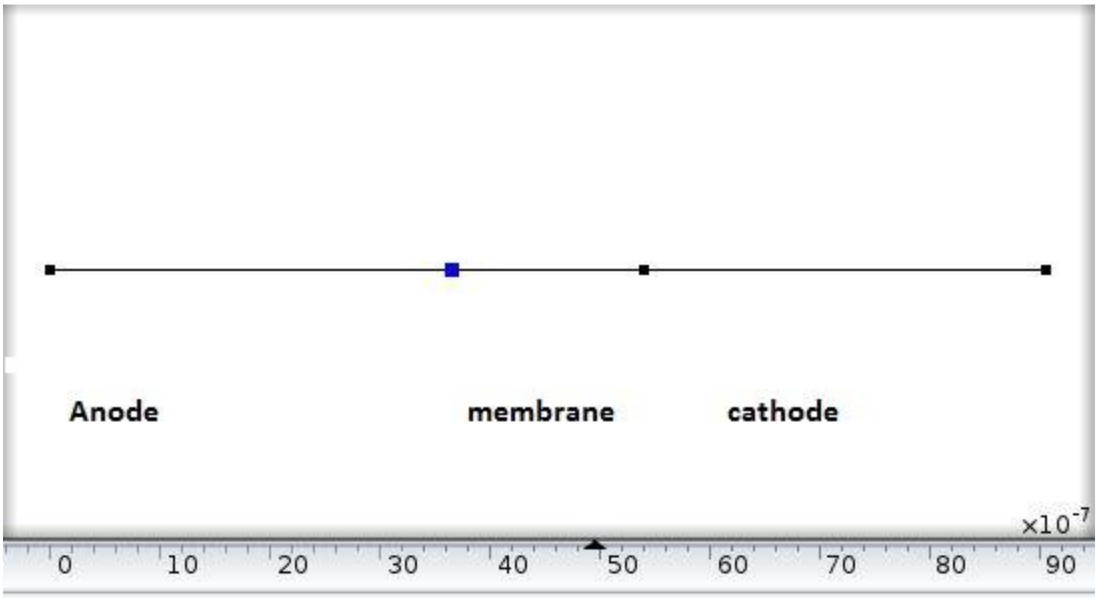

Fig 3: Geometry of 1-D PEMFC model

3.1 Geometry

Anode thickness 0.0365cm

Cathode thickness 0.0365cm

3.2 Time dependent equation

$$e_a \frac{\partial^2 \lambda}{\partial t^2} + d_a \frac{\partial \lambda}{\partial t} + \nabla . \Gamma = f \qquad (3.2)$$

3.2.1 Boundary conditions

Zero Flux

$$-n.\Gamma = 0 \qquad (3.3)$$

Boundary condition 1

$$-n.\Gamma = g - q\,\lambda \qquad (3.4)$$

Boundary condition 2

$$-n.\Gamma = g - q\,\lambda$$

Where g is Boundary Flux/Source and q is Boundary Absorption /ImpedanceTerm

3.3. Transport of species at anode

Time dependent equations

$$\rho\frac{\partial w_i}{\partial t} + \nabla.j_i = R_i \quad (3.5)$$

$$N_I = j_i \quad (3.6)$$

$$j_i = \left(-\rho w_i \sum_k D_{ik} d_k + D_i^T \frac{\nabla T}{T}\right) \quad (3.7)$$

$$d_k = \nabla X_k + \frac{1}{p_A}[(X_k - w_k)\nabla p_A] \quad (3.8)$$

$$X_k = \frac{w_k}{M_k} M_n \quad (3.9)$$

$$M_n = \left(\sum_i \frac{w_i}{M_i}\right)^{-1} \quad (3.10)$$

Mixture density for Ideal gas

$$\rho = \frac{P_A M_n}{RT} \quad (3.11)$$

No flux equation for Time dependent condition

$$-n.N_i = 0 \quad (3.12)$$

3.3.1 Initial conditions at Anode

Initial values of Mass fraction at anode

$H_2 = 0.5$

$H_2O = 0.5$

Inflow condition for Time dependent condition

$w_i = w_{0,j}$

Flux for transport of species at anode

$$-n.N_i = N_{0,j} \tag{3.13}$$

Inward flux for Hydrogen given by

$$N_{0,Hydrogen} = -\left(\frac{J}{2F} * molecular\ weight\ of\ Hydrogen\right) \tag{3.14}$$

3.4 Transport of species at cathode

Time dependent equations

$$\rho\frac{\partial w_i}{\partial t} + \nabla.j_i = R_i \tag{3.15}$$

$$N_I = j_i \tag{3.16}$$

$$j_i = \left(-\rho w_i \sum_k D_{ik} d_k + D_i^T \frac{\nabla T}{T}\right) \tag{3.17}$$

$$d_k = \nabla X_k + \frac{1}{p_A}[(X_k - w_k)\nabla p_A] \tag{3.18}$$

$$X_k = \frac{w_k}{M_k} M_n \tag{3.19}$$

$$M_n = \left(\sum_i \frac{w_i}{M_i}\right)^{-1} \tag{3.20}$$

Mixture density for Ideal gas

$$\rho = \frac{P_A M_n}{RT} \tag{3.21}$$

No flux equation for Time dependent condition

$$-n.N_i = 0 \tag{3.22}$$

3.4.1 Initial conditions for cathode

Mass fraction of water and oxygen are

$H_2o = 0.065$

$O_2 = 0.1739$

3.4.2 Inflow condition for Time dependent condition

$w_i = w_{0,j}$

Flux for transport of species at cathode

$$-n.N_i = N_{0,j} \tag{3.23}$$

Inward flux for Oxygen given by

$$N_{0,Oxygen} = -\left(\frac{J}{4F} * molecular\ weight\ of\ Oxygen\right) \tag{3.24}$$

3.5. Mesh

Statistics of Mesh are

Edge elements : 102

Vertex elements : 4

Domain elements statistics

Number of elements : 102

Element length ratio : 0.9829

Mesh length : 9.05E-6 m

Maximum growth rate : 1

Average growth rate :1

Chapter 4 : Results & Discussion

4.1 Results of steady state model of PEMFC

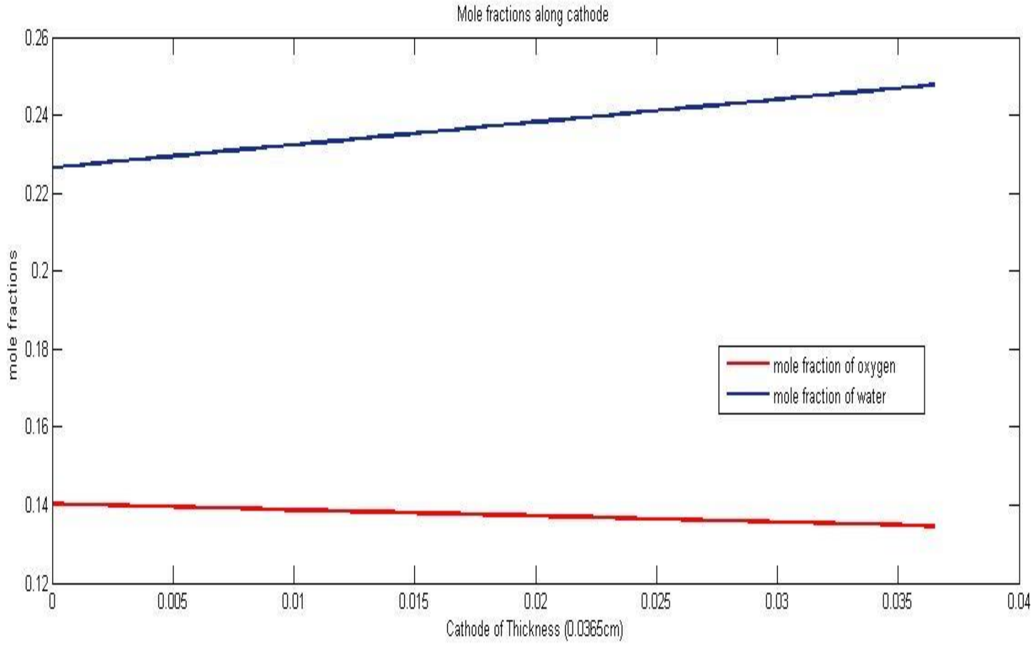

Fig 4.1 : molefraction of oxygen , water vs cathode thickness

In the above figure mole fraction of oxygen at cathode ,interface 4 (X_{O4}) , mole fraction of water at cathode , interface 4 (X_{w4}) as initial values to calculate mole fraction of oxygen at cathode ,interface 3 (X_{O3}) and mole fraction of water at cathode , interface 3 (X_{w3}) .

X_{O3} , X_{w3} will be used in calculation of λ(membrane water content)

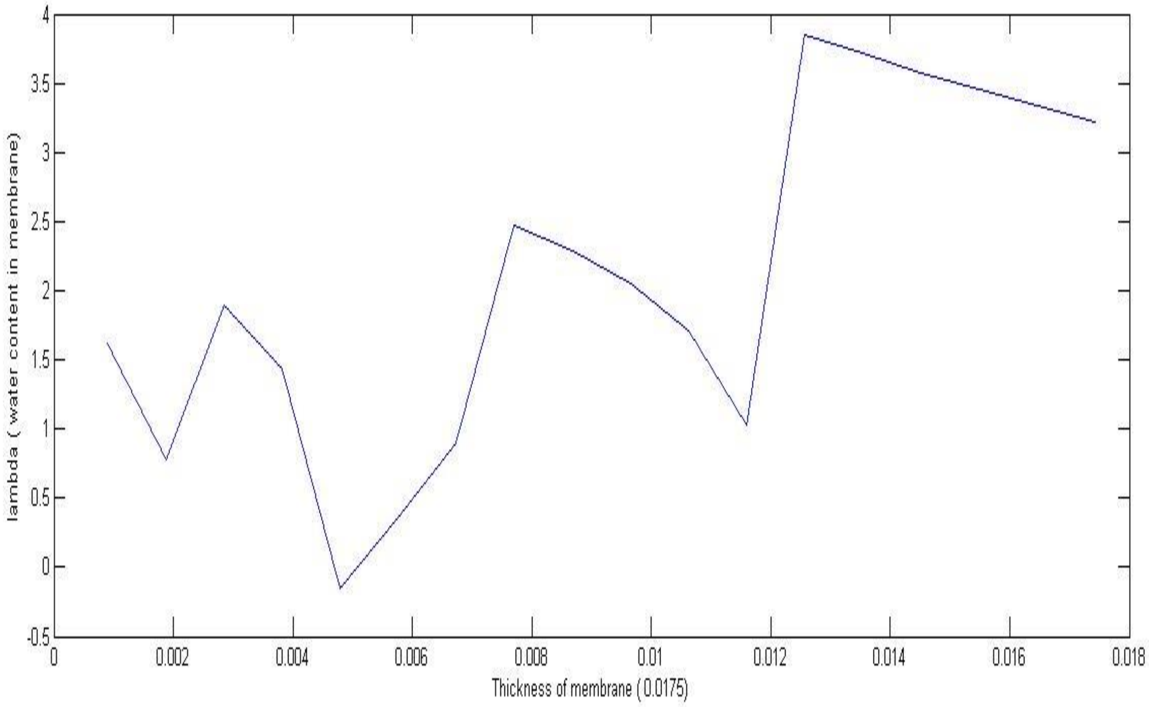

Fig4.1.2:watercontent(λ) vs thickness of membrane(0.0175cm)

The water content would be affected by drag coefficient η_{drag} and concentration difference of water formation from cathode to anode that is $N_{w, diff}$.

4.1.3 Input parameters for steady state model of PEMFC

Sno	Input parameters
1.	Voc(open circuit) =1.1 v
2.	Membrane thickness =0.0175cm
3.	Anode thickness = 0.0365cm
4.	Cathode thickness = 0.0365 cm
5.	Tcell =353 k
6.	Pa(anode pressure) = 3 atm
7.	Pc(cathode pressure) = 3atm
8.	Xon=0.21

4.1.4 Computed values of steady state model of PEMFC

Sno	Computed valued by Springer	My values
1.	Xw1=0.1015 Mole fraction of water at interface 1	Xw1=0.1015
2.	Xw2=0.1013 Mole fraction of water at interface 2	Xw2=0.1013
3.	Xw3=0.2327	Xw3=0.2478

	Mole fraction of water at interface 3	
4.	Xo3=0.1329 Mole fraction of oxygen at interface 3	Xo3=0.1346
5.	Xo4 =0.1403 Mole fraction of oxygen at interface 4	Xo4 =0.1403
6.	Xw4=0.2264 Mole fraction of water at interface 4	Xw4=0.2264
7.	Rmem =0.2 Ώ Resistance of membrane	Rmem=0.00420

4.2 Results of unsteady state model of PEMFC

Lambda (water content inside membrane) with respect to space at t=0 seconds.

The Unsteady state equations derived for this model is been used to understand the water content (lambda) inside membrane equation of PEMFC.

At every point of time in the range of 0 to 1, with interval of 0.1 is determined , The graphs are given below

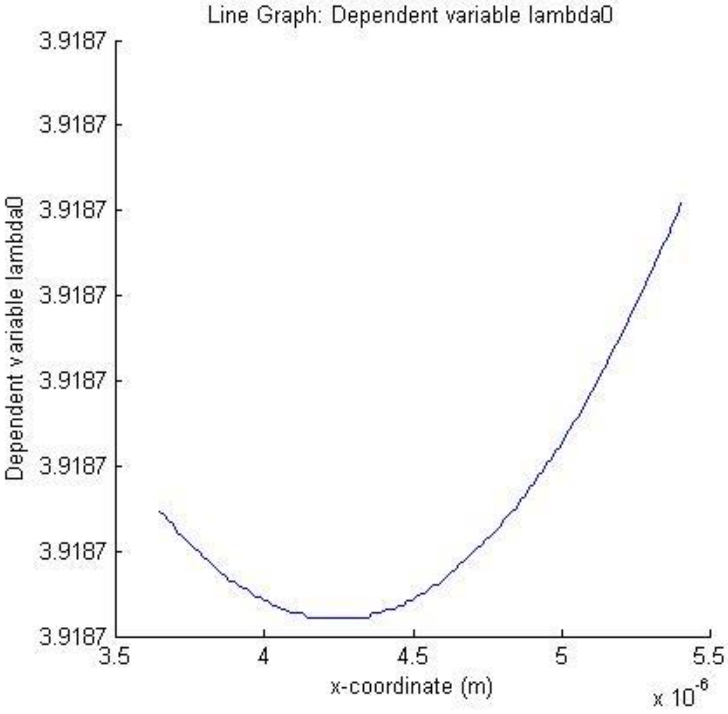

Fig 4.2.1 lambda vs space at time t=0 seconds

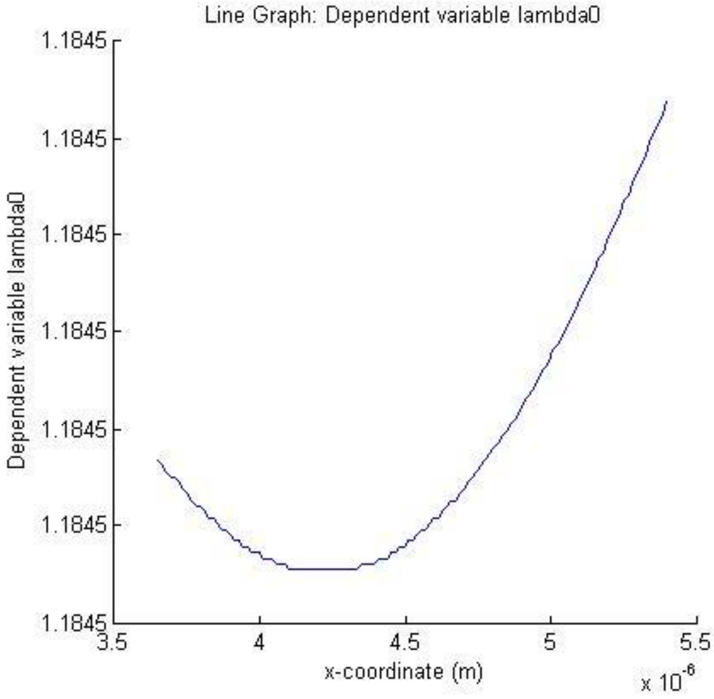

Fig 4.2.2 lambda vs space at time t=0.1 seconds

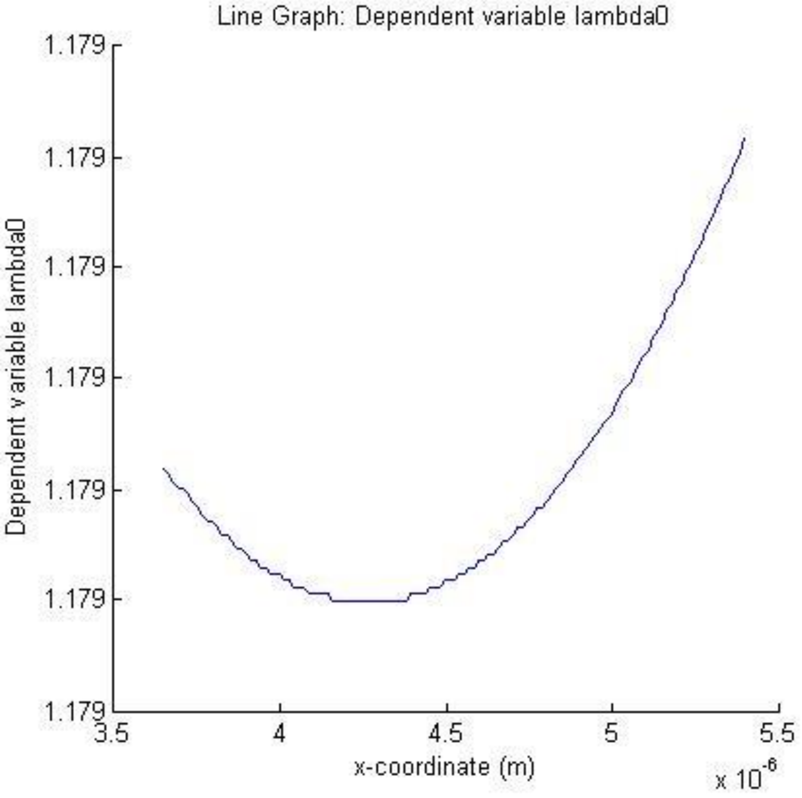

Fig 4.2.3 lambda vs space at time t=0.2 seconds

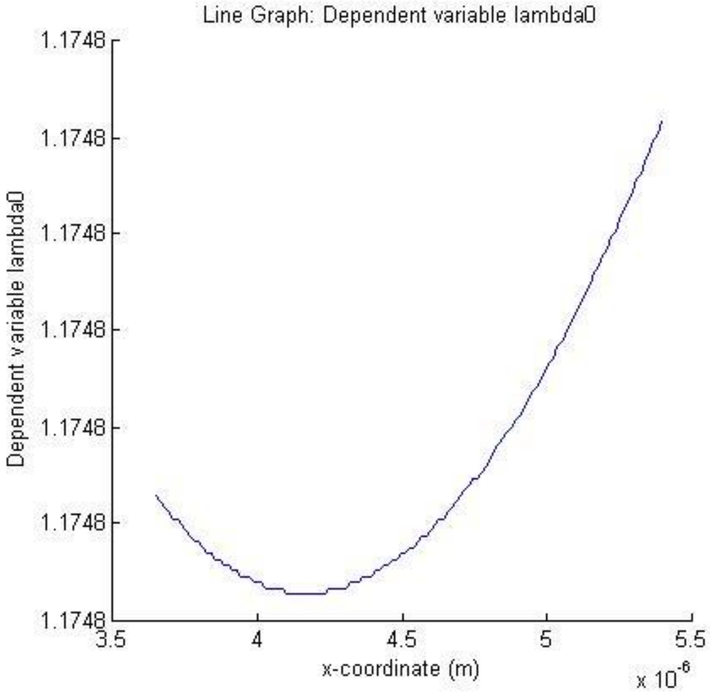

Fig 4.2.4 lambda vs space at time t=0.3 seconds

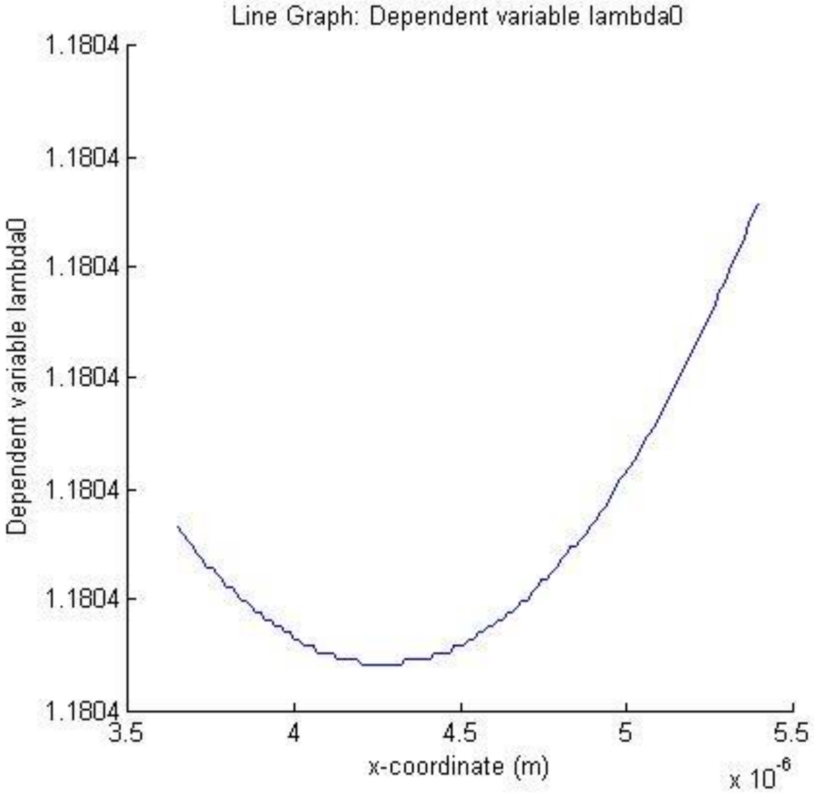

Fig 4.2.5 lambda vs space at time t=0.4 seconds

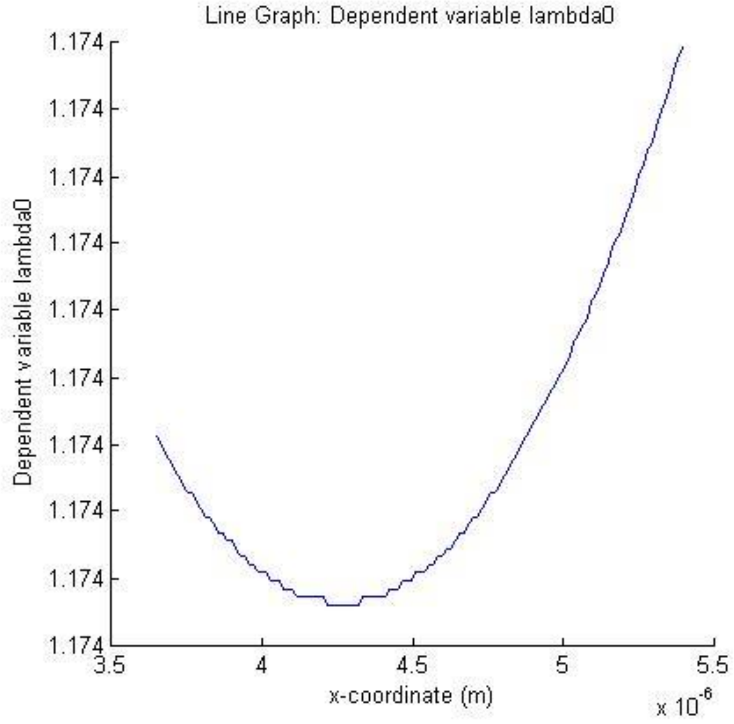

Fig 4.2.6 lambda vs space at time t=0.5 seconds

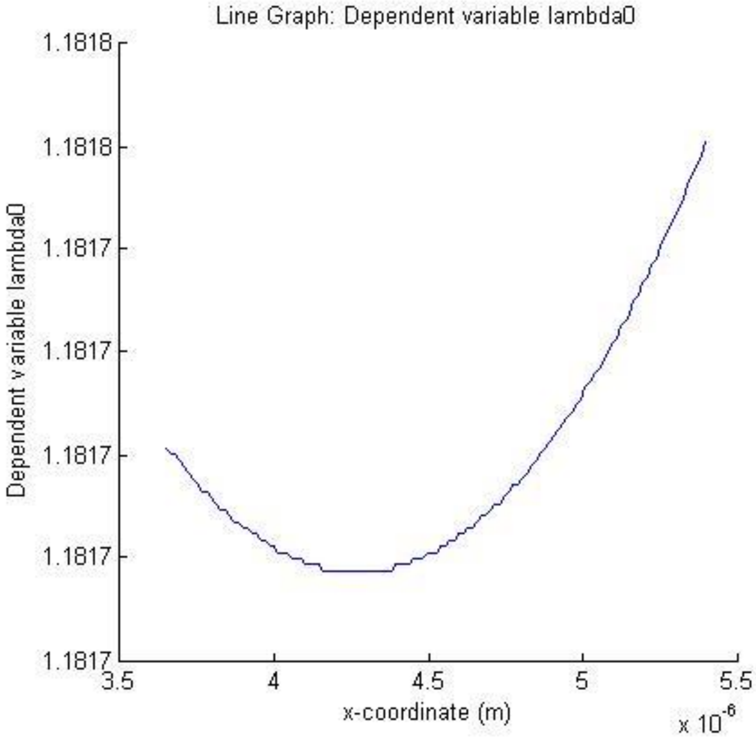

Fig 4.2.7 lambda vs space at time t=0.6 seconds

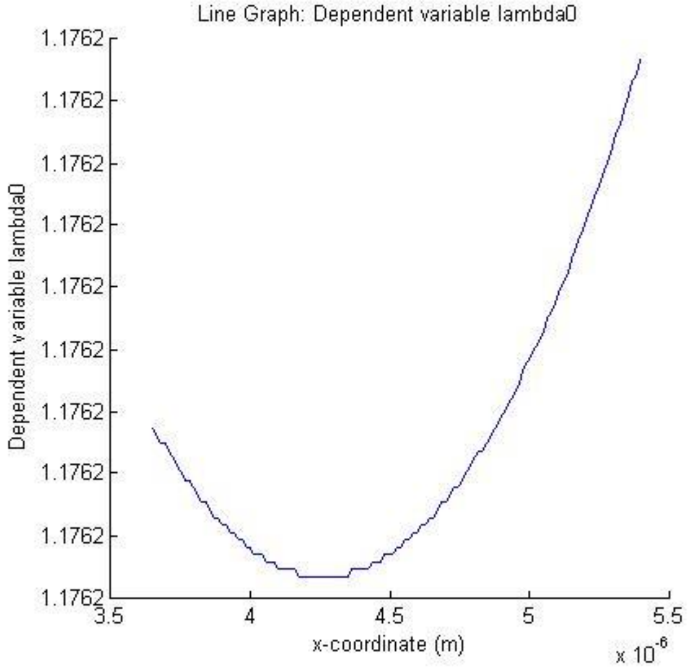

Fig 4.2.8 lambda vs space at time t=0.7 seconds

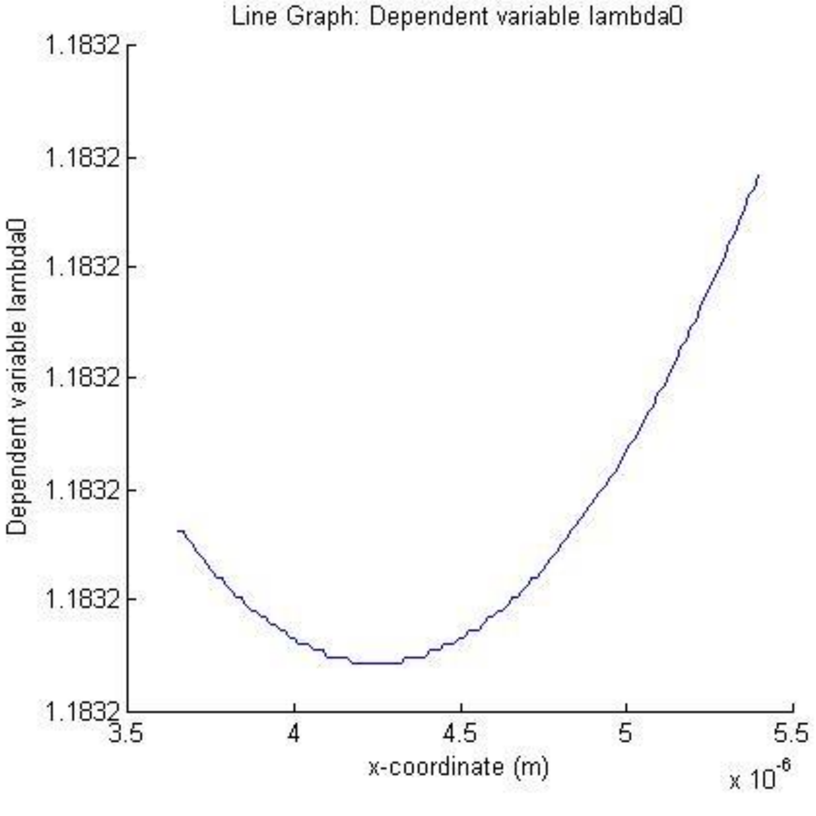

Fig 4.2.9 lambda vs space at time t=0.8 seconds

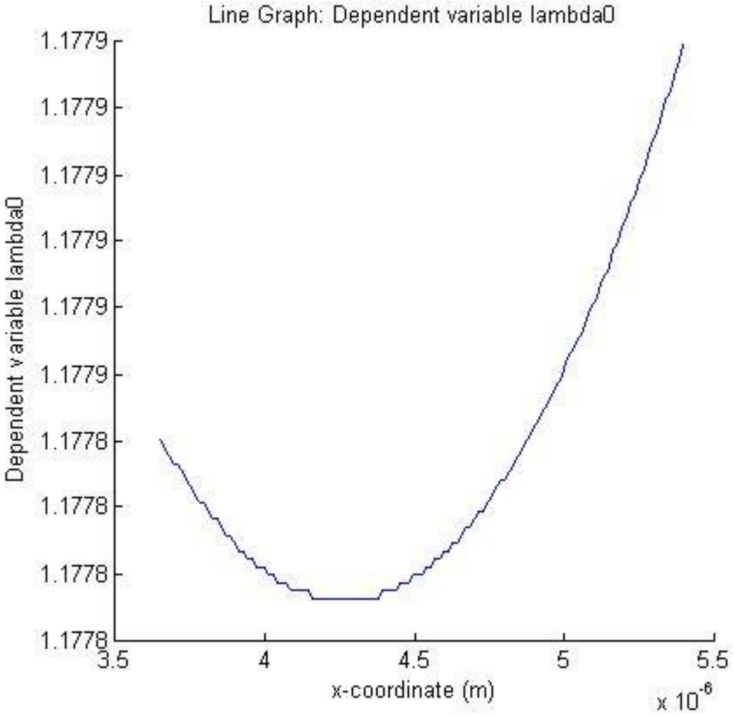

Fig 4.2.10 lambda vs space at time t=0.9 seconds

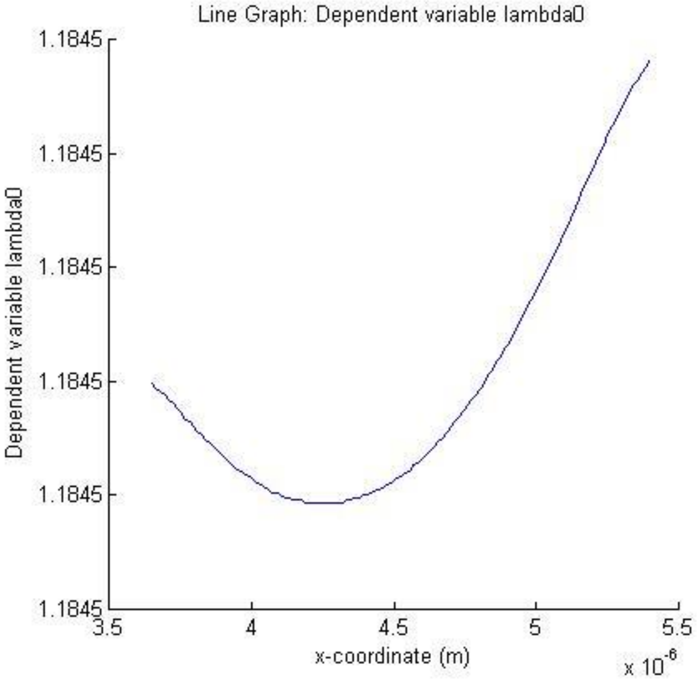

Fig 4.2.11. lambda vs space at time t=1 second

4.3. Mole fraction with respect to space at anode

Hydrogen in saturated humidified form is given as inlet at anode , it reacts with oxygen from cathode inlet to give water at cathode . At every point of time in the range 0 to 1 seconds with increase of 0.1 second is considered , The following are the lines are obtained at different time intervals

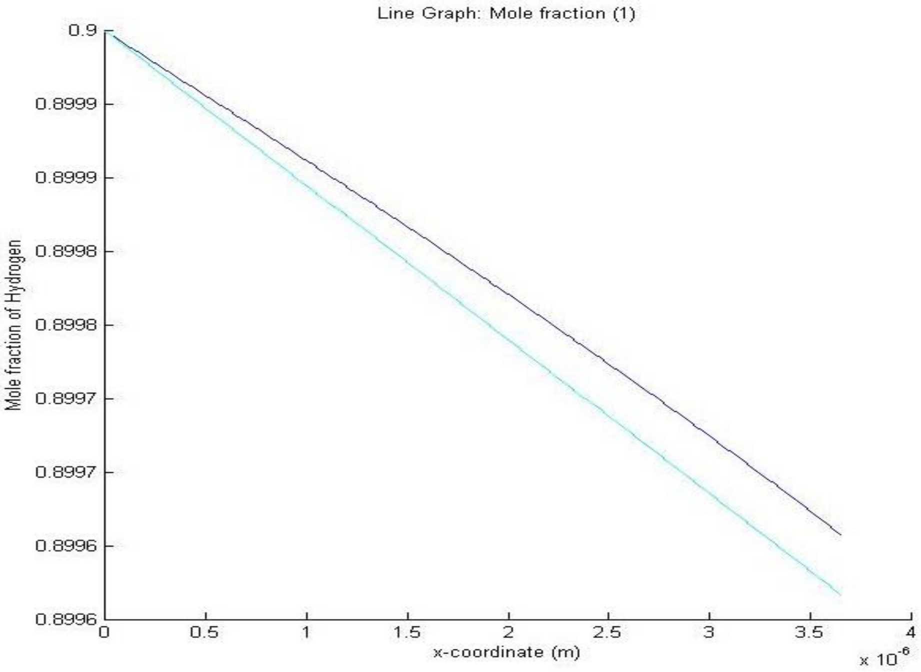

Fig 4.3.1 Mole fraction of Hydrogen at Anode with respect to space coordinate at different time intervals from 0 to 1 second with increment of 0.1 second

4.3.2 Mole fraction of water with respect to space at anode

There are two species at anode , where humidified Hydrogen is given as inlet .

Water and Hydrogen are the two species we will be considering for mole fraction profile . At every point of time in the range 0 to 1 seconds with increase of 0.1 second is considered , The following are the lines are obtained at different time intervals

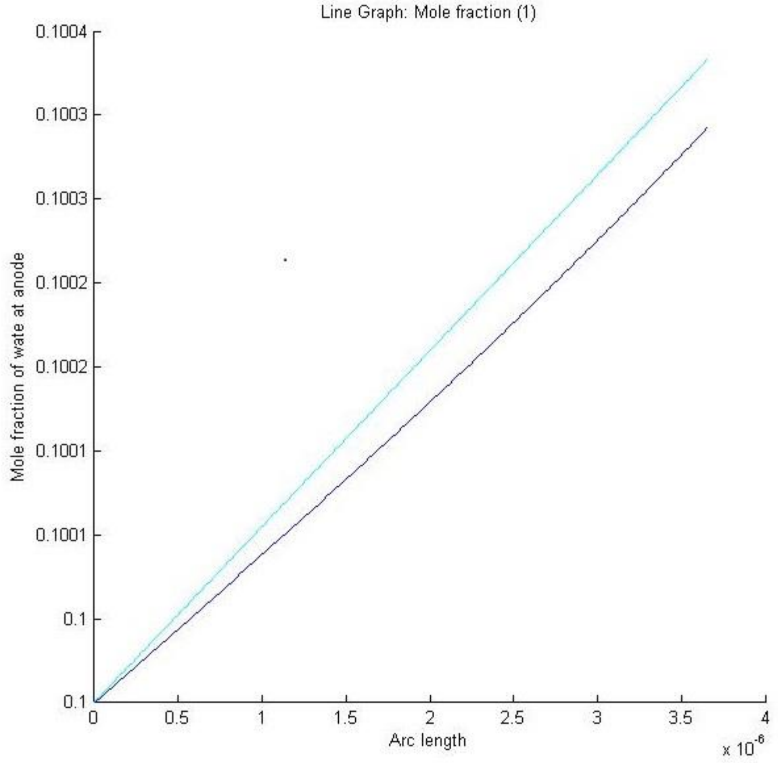

Fig 4.3.2 : Mole fraction of water with respect to space coordinate at anode at different time intervals from 0 to 1 second with increment of 0.1 second

4.4 Mole fraction with respect to space coordinate at cathode

Humidified air is given as inlet for cathode , So we will be considering three species at cathode . The constituents of air are oxygen 21% , nitrogen 79% .Oxygen , nitrogen and water are the three species used at cathode . At every point of time in the range 0 to 1 seconds with increase of 0.1 second is considered , The following are the lines are obtained at different time intervals

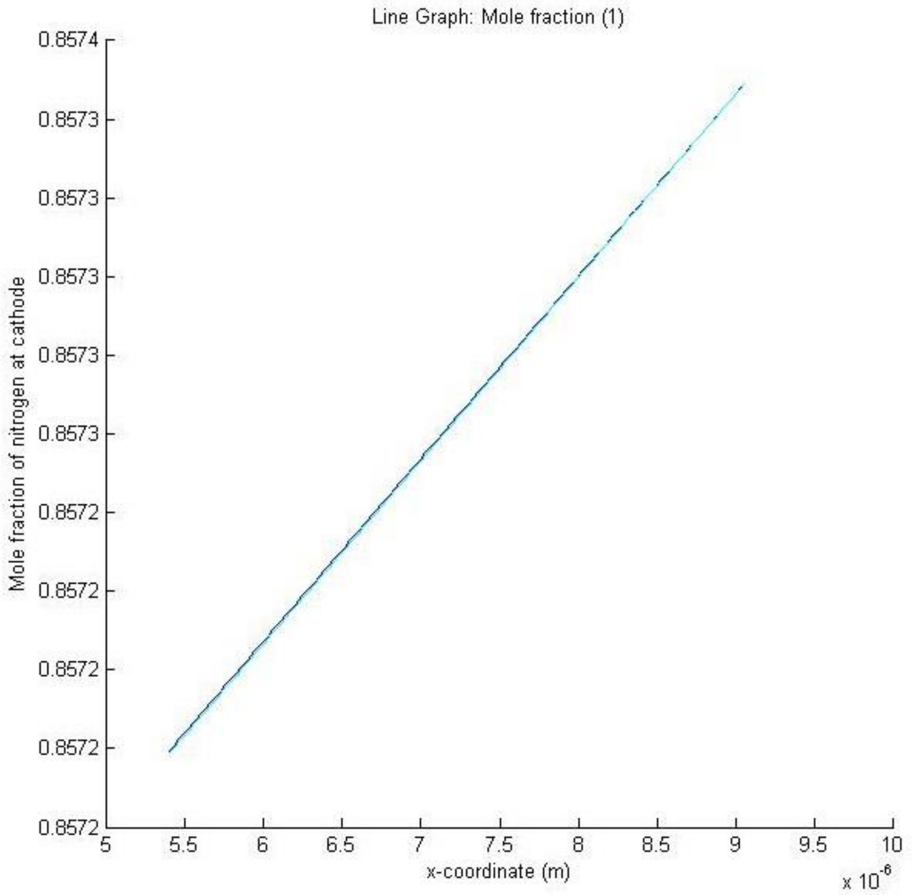

Fig 4.4.1 Mole fraction of Nitrogen with respect to space coordinate at cathode at different time intervals from 0 to 1 second with increment of 0.1 second

4.4.2 Mole fraction of Water with respect to space coordinate at cathode

The primary reaction of PEMFC , where Humidified Hydrogen at anode and Humidified air at cathode react together leading to the formation of water at cathode. At every point of time in the range 0 to 1 seconds with increase of 0.1 second is considered , The following are the lines are obtained at different time intervals

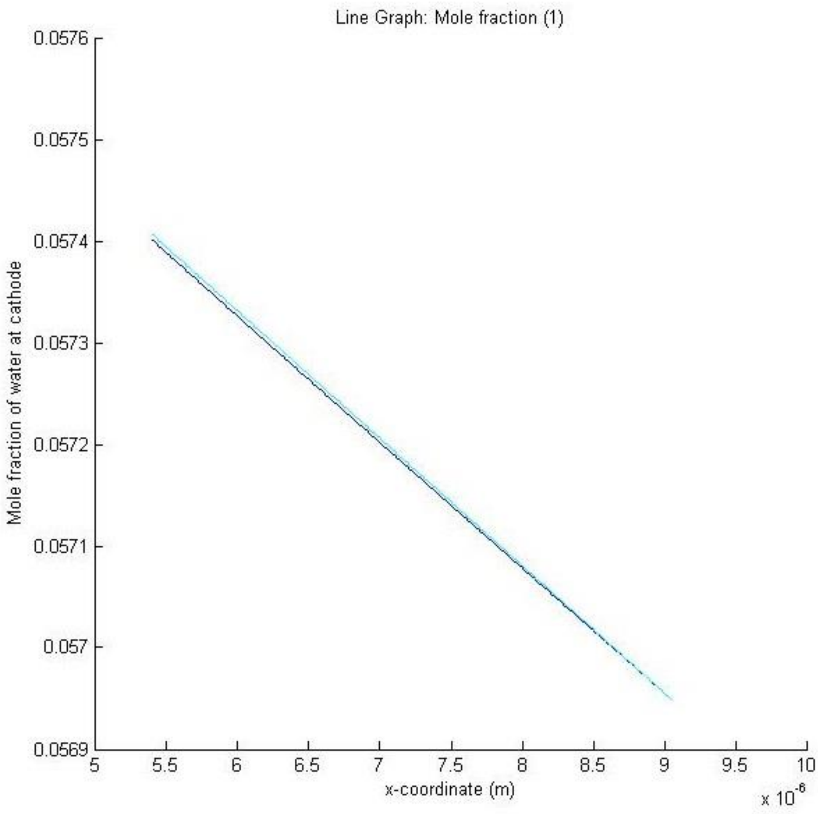

Fig 4.4.2 Mole fraction of water with respect to space inside cathode at different time intervals from 0 to 1 second with increment of 0.1 second

4.4.3 Mole fraction of Oxygen with respect to space coordinate at cathode

Oxygen in the form of air is given as inlet , due to reaction inside PEMFC the concentration of oxygen and hydrogen decreases and water concentration increases along the length of PEMFC . At every point of time in the range 0 to 1 seconds with increase of 0.1 second is considered , The following are the lines are obtained at different time intervals

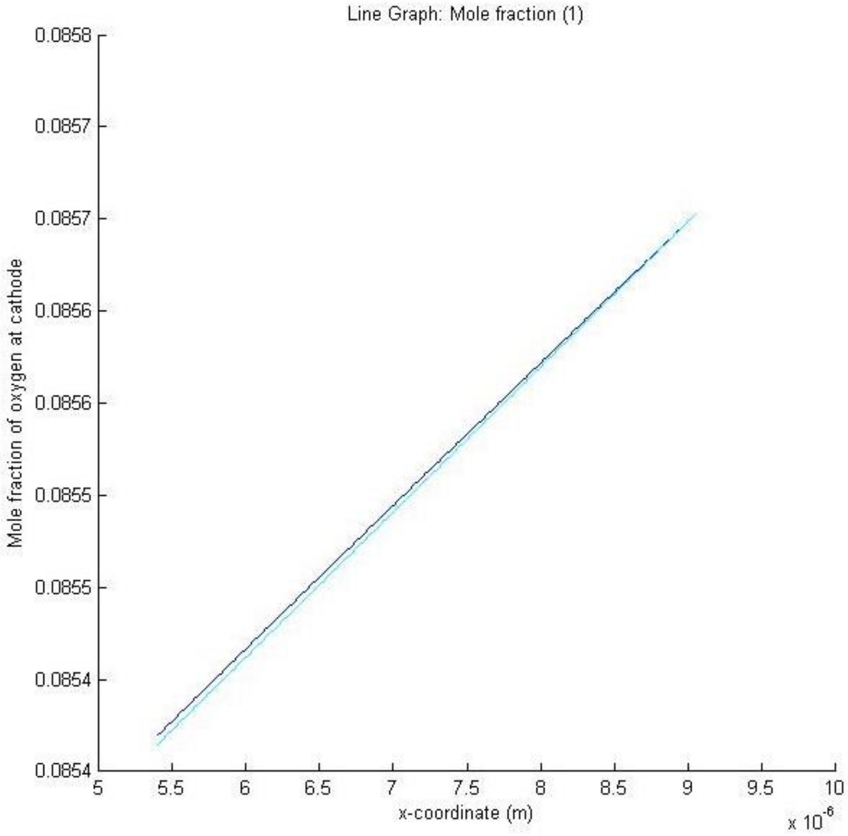

Fig 4.4.3 Mole fraction of oxygen with respect to space inside cathode at different time intervals from 0 to 1 second with increment of 0.1 second

Chapter 5 :References

1. Soc, J. E., The, A., Society, E., Springer, T. E., Zawodzinski, T. A., & Gottesfeld, S. (1993). Polymer Electrolyte Fuel Cell Model, *138*(8), 2334–2342.
2. Bird , R.B., Stewart,W.E., and Lightfoot,E.N.*Transport Phenomena*,John Wiley& Sons,New York ,U.S.A, 2nd edition ,2009.
3. O'Hayre, R.,Cha , W.S., Colella,W.,Prinz,B.F.*Fuel Cell Fundamentals* , John Wiley Sons,2nd edition,2009.
4. James Larmine , Andrew Dicks *Fuel Cell Systems Explained* ,John Wiley Sons, 2nd edition ,2003.
5. Bei Gou , Woon Ki Na , Bill Diong. *Fuel Cells Modeling , Control , and Applications* CRC Press ,2010.
6. David P.Wilkinson , Jiujun Zhang , Rob Hui , Jeffrey Fergus , Xianguo Li *Proton Exchange Membrane Fuel Cells , Materials Properties and Performance* CRC Press ,2010 .
7. Frano Barbir *PEM Fuel Cells: Theory and Practice* Elsevier Academic Press ,2005 .
8. Jay T. Pukrushpan , Anna G.Stefanopoulou , Huei Peng *Control of Fuel Cell Power Systems* , Springer-Verlag , 2nd edition , 2005.
9. Ahmed, S., & Chmielewski, D. J. (2009). Dynamics and control of membrane hydration in a PEMFC. *2009 American Control Conference, 2,* 2648–2653.
10. Bavarian, M., Soroush, M., Kevrekidis, I. G., & Benziger, J. B. (2010). Mathematical Modeling, Steady-State and Dynamic Behavior, and Control of Fuel Cells: A Review †. *Industrial & Engineering Chemistry Research*, *49*(17), 7922–7950.
11. Bothe, D. (n.d.). On the Maxwell-Stefan approach to multicomponent diffusion Continuum Mechanical Modeling of Multicomponent Fluids, 1–13.
12. Dawn, M., & Mark, W. (2013). Golbert, J., & Lewin, D. R. (2004). Model-based control of fuel cells: *Journal of Power Sources*, *135*(1-2), 135–151.
13. Huang, B., Qi, Y., & Murshed, M. (2011). Solid oxide fuel cell: Perspective of dynamic modeling and control. *Journal of Process Control, 21*(10), 1426–1437.
14. Liu, X., Schnell, S. K., Simon, J.-M., Bedeaux, D., Kjelstrup, S., Bardow, A., & Vlugt, T. J. H. (2011). Fick diffusion coefficients of liquid mixtures directly obtained from equilibrium molecular dynamics. *The Journal of Physical Chemistry. B*, *115*(44), 12921–9.
15. Makrodimitri, Z. a, Unruh, D. J. M., & Economou, I. G. (2011). Molecular simulation of diffusion of hydrogen, carbon monoxide, and water in heavy n-alkanes. *The Journal of Physical Chemistry. B*, *115*(6), 1429–39.

16. Meidanshahi, V., & Karimi, G. (2012). Dynamic modeling, optimization and control of power density in a PEM fuel cell. *Applied Energy*, *93*, 98–105.
17. Riascos, L. a. M. (2008). Relative humidity control in polymer electrolyte membrane fuel cells without extra humidification. *Journal of Power Sources*, *184*(1), 204–211.
18. Secanell, M., Wishart, J., & Dobson, P. (2011). Computational design and optimization of fuel cells and fuel cell systems: A review. *Journal of Power Sources*, *196*(8), 3690–3704.
19. Soc, J. E., The, A., Society, E., Springer, T. E., Zawodzinski, T. A., & Gottesfeld, S. (1993a). Polymer Electrolyte Fuel Cell Model, *138*(8), 2334–2342.
20. Tolj, I., Bezmalinovic, D., & Barbir, F. (2011). Maintaining desired level of relative humidity throughout a fuel cell with spatially variable heat removal rates. *International Journal of Hydrogen Energy*, *36*(20), 13105–13113.
21. Transfer, N. H. (2007). Multicomponent Mass Transfer : Basic Physics and Engineering Modeling.
22. Vasu, G., & Tangirala, a. K. (2008). Control-orientated thermal model for proton-exchange membrane fuel cell systems. *Journal of Power Sources*, *183*(1), 98–108.
23. Wong, K. H., Loo, K. H., Lai, Y. M., Tan, S. C., & Tse, C. K. (2011). A theoretical study of inlet relative humidity control in PEM fuel cell. *International Journal of Hydrogen Energy*, *36*(18), 11871–11885.
24. Zhang, J., Tang, Y., Song, C., Xia, Z., Li, H., & Wang, H. (2008). PEM fuel cell relative humidity (RH) and its effect on performance at high temperatures. *Electrochimica Acta*, *53*(16), 5315–5321.
25. Riascos, L. a. M. (2008). Relative humidity control in polymer electrolyte membrane fuel cells without extra humidification. *Journal of Power Sources*, *184*(1), 204–211.
26. Tolj, I., Bezmalinovic, D., & Barbir, F. (2011). Maintaining desired level of relative humidity throughout a fuel cell with spatially variable heat removal rates. *International Journal of Hydrogen Energy*, *36*(20), 13105–13113.
27. Wong, K. H., Loo, K. H., Lai, Y. M., Tan, S. C., & Tse, C. K. (2011). A theoretical study of inlet relative humidity control in PEM fuel cell. *International Journal of Hydrogen Energy*, *36*(18), 11871–11885.