



A Numerical Study of Thermal Stress in Nafion and PTFE Membranes of Fuel Cell

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Abstract

Membrane is necessarily required for the chemical reaction in fuel cell. Periodic variation in the temperature generates thermal stress during the process affecting the performance of membrane. In this paper, thermal stress produced in fuel cell having Nafion and PTFE membrane and its effect on proton and water transport are studied by simulation. For the purpose governing equations developed by other researchers were used for modelling and simulation. From the study, the use of PTFE membrane over Nafion reduces thermal stress by 44%.

Keywords: Fuel cell, Nafion and PTFE membrane, Thermal Stress, Proton and water transport.

1. Introduction

An electrochemical reaction in the fuel cell between the oxidizing agents (hydrogen, CH₄ etc) with oxygen converts the chemically stored energy into electrical power. Fuel cell can be broadly categorized based on the working principle and fuel type utilized, but the common components among the different fuel cells are a cathode, an anode and an electrolyte which supports positively charged hydrogen protons (ions) to migrate between the two sides of the fuel cell. Oxidation reactions at the anode cause hydrogen to generate positively charge hydrogen ions (protons) and electrons. After the reaction, proton circulates from an anode to cathode through the medium electrolyte. In the mean while from an external circuit electrons are collected from an anode to the cathode generating direct current electricity. In cathode area, another set of catalyst causes hydrogen ions, electrons, and oxygen to react to form water.

Thermal stress is one of the types of mechanical stresses developed in the system when different parts in the fuel cell are not free to expand or contract in response to the change in temperature. Starting time for PEMFC is 30-35 seconds and after 40 seconds of operation the temperature stabilizes resulting in generation of stresses. Thus the number of moles of proton and water to be transported from anode to cathode exceeds or falls below with respect to standard value.

Number of studies has been conducted on thermal stress for fuel cell, its distribution and its effect on the performance of the fuel cell with fluctuating temperature and selection of membrane based on operating conditions. Min Xu et.al, [1] numerically investigated the high temperature proton exchange membrane fuel cell. Applying the computational fluid dynamics and combined finite element techniques, they investigated the outcome of gas diffusion layer compression and intrusion on the behaviour of phosphoric acid doped polybenzimidazole membrane (PBI). The damage to planar solid fuel cell by thermal stress and cycling was

explained by A. Atkinson and B. Sun [2]. The result was analysed by X-Ray diffraction and simple thermo electric analogy. Jiamiao Xie [3], studied on optimisation anode function layer to minimise the anode axial stress, electrolyte compressive stress. James B Robinson [4] studied on thermal gradients developed due to start up, shutdown on YSZ/Ni SOFC anode fuel cells and it was analysed using synchrotron X-ray diffraction.

P. Pianko [5], 3-d models were developed and investigated the flow channels fuel cell arrangements to calculate the thermal stress in SOFC. S.A. Hajimola came up with a result that guides to keep the constant working temperature in order to avoid the thermal stress. Min Xu [6], studied on thermal stress generated from difference in temperature and mismatch in mechanical properties can result in crack damage. J. Malzbender [7], worked on the residual stress developed between the individual layers of fuel cell and mismatch in the thermo elastic properties resulted in wrapping of unconstrained cells. S.M Javid Zaidi [8] conducted a performance test on Dow membrane (Dow Chemical Co.), PFI membrane and modified perfluorinated ionomer membrane and compared its performance results. Thus simulating and analysing the thermal stress is important for optimizing the fuel cell system performance.

2. Types of Membrane Used

2.1. About Membrane:

The chemical reaction involving oxidation and reduction inside the fuel cell takes place by membrane's participation. This is the main reason behind the lot of work carried out for the improvement of membrane in terms of its performance.

The required properties of the membrane to be used as a proton conductor in a fuel cell are listed in the following:

- Electro-chemical, chemical, thermal and hydrolytic stability in various operating situations.

- At high temperatures of operation, membrane should possess high water uptake capacity [9].
- Bonding requirements of membrane electrode assembly with compatible chemical properties.
- With zero electronic conductivity and minimal resistive losses, membrane should be able to conduct proton and facilitation for rapid electrode kinetics.

2.2. Nafion Membrane:

It is a tetra fluoro sulfonated ethylene based fluoro-polymer-co-polymer. Each fluoro-vinyl ether chains are completed with sulfonate groups bonded to tetra fluoro-ethylene results in good ionic properties. Nafion has earned an appreciable consideration as a proton conductor for PEMFC due to mechanical stability and distinguished thermal conductivity. Nafion membranes are available in different sizes and thicknesses. These are represented by alphabet 'N', continued by a 3 or 4 digit numbers. The first 2 digits after N portraits equivalent weight of the membrane divided by 100, and the remaining digit which is left is the thickness of membrane in mills and 1 mill is equivalent to 0.0254mm. Availability of membrane with varying thickness is 2, 3, 5, 7, and 10 mills.

Characteristics of Nafion membrane:

- Good cations conducting property suits for membrane application.
- Resistive for chemical attack. At atmosphere conditions alkali metals like sodium can degrade Nafion membrane.
- High operating temperature ranging up to 190°C.
- Sulfonic acid groups, fluorinated ethylene and stabilized polymer matrix leads the Nafion membrane to strong acid.
- High and selective water permeability level.

Proton conductivity is a percolation of temperature and hydration state and its maximum value for Nafion membrane is 0.2S/cm.

2.3. Poly Tetra Fluoro Ethylene:

It is a synthetic fluoro-polymer of tetra fluoro ethylene. The best known example is Teflon. PTFE is completely made up of carbon and fluorine, hence it is a fluorocarbon solid and noticing property of this compound is high molecular weight. Nature of this membrane is hydrophobic, either water or water-containing substances. Compared to any solids, this membrane has lowest coefficient of friction.

Table I: Properties of PTFE Membrane

Properties(Unit)	Magnitude
Membrane Density(kg/m ³)	2150 - 2200
Glass point temperature(K)	390
Melting temperature (K)	590-600
Young's modulus(Gpa)	0.4995
Yield strength(Mpa)	23-24
Bulk resistivity (Ω.m)	10 ¹⁶
Friction co-efficient	0.06-0.11
Di-electric constant	$\epsilon = 2.11, \tan(\delta) < 5$
Di-electric constant for (60 Hz)	$\epsilon = 2.12, \tan(\delta) < 2$
Di-electric strength for (1 MHz)	60-80 MV/m
Co-efficient of thermal expansion(K ⁻¹)	112-125*10 ⁻⁶

3. Methodology

The PEMFC virtual model is simulated using Simulink software in order to determine the thermal stresses distribution. The assumptions considered for the development of virtual model are given below.

- Laminar flow in control volume.

- Working fluid obeys ideal gas law and no external work is done on the system.
- The potential and kinetic energies of the gas molecules are ignored.
- Convective heat transfer coefficients and specific heats of gases inside the system are constant.
- Properties of anode, cathode and membrane of fuel cell are considered uniform with temperature.
- Temperature gradient and water concentration disciplines the water transport in membrane.

3.1 Mathematical Model:

3.1.1 Proton Transport:

Hydrophilic sulphonic acid chains in the Nafion membrane absorb water after hydration and builds up transportation of proton by the following process. Proton transport [10] occurs by diffusion at low hydration levels. At peak levels of hydration, proton hopping phenomenon takes place due to increased connectivity between SO₃⁻ groups. Therefore membrane hydration is exigently an important parameter.

$$\lambda = 0.044 + 17.7\Phi - 39.86\Phi^2 + 36.1\Phi^3. \text{ Where } 0 \leq \Phi \leq 1, \Phi = p/p_{\text{sat}} \quad (1)$$

By assuming that the reactant species acts as an ideal gas, membrane water content is proportional to relative humidity and water vapour activity is replaced by relative humidity. Number of water molecules per sulfonic group is defined as water content in the membrane or percentage of humidification, (H₂O/ SO₃⁻ H⁺).

3.1.2 Water Transport:

Electro-osmotic drag, Diffusion, Back diffusion, hydraulic pressure and Thermo osmosis are the five different mechanisms of water transport. Summing up all the water transport mechanisms and specifying the flow from the anode to cathode as positive. The net flow rate of water [10] through the membrane is given by:

$$N_{\text{H}_2\text{O}}^{\text{memb}} = N_{\text{H}_2\text{O}}^{\text{eodg}} \pm N_{\text{H}_2\text{O}}^{\text{bdn}} \pm N_{\text{H}_2\text{O}}^{\text{hpr}} + N_{\text{H}_2\text{O}}^{\text{tmp}} + N_{\text{H}_2\text{O}}^{\text{dif}} \quad (2)$$

The dominant mechanisms considered for the calculations are electro-osmotic drag, back diffusion and diffusion.

1. Electro-Osmotic drag:

The anode GDL permits hydrogen to reactive zone to react in the catalyst layer upon which protons (H⁺) and electrons (e⁻) are separated. Electrons are conducted to the external circuit and the protons get migrated to cathode through ion conducting membrane. Depending on the hydration level of the membrane, the migrating proton drags the nearby water molecules along with them to cathode. This process is electro-osmotic drag transport. Co-efficient of electro-osmotic drag defined as amount of water molecules dragged or transported per proton. Specifically, this process occurs from anode to cathode. Molar flow rate for water [10] is given by,

$$N_{\text{H}_2\text{O}}^{\text{eodg}} = (n_d * (I/F)) \quad (3)$$

The humidification or water uptake range is $15 \leq \lambda_w \leq 25$, and as per study, co-efficient of electro osmotic drag decreases linearly with respect to water content in the membrane.

$$n_d = (2.5 * (\lambda_w / 22)) \quad (4)$$

2. Back diffusion:

The coagulated result of water generation due to chemical reaction between hydrogen and oxygen at cathode and due to electro osmotic drag tends to flood the cathode area and dry out anode.

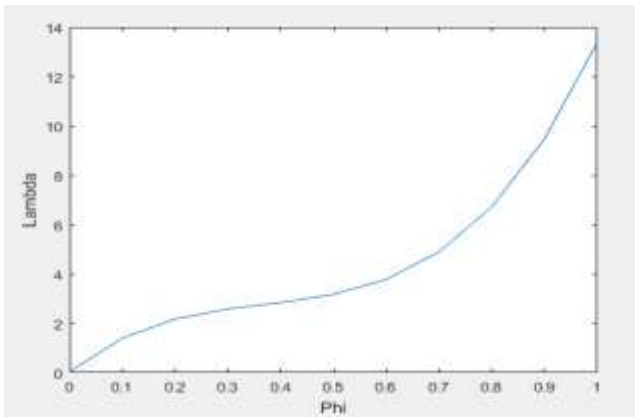


Fig 2: Graphical representation of Proton Transport in the membrane

The plot shown in fig 4 clearly explains electro osmotic drag is moderately proportional to water uptake capacity. One proton can carry 25 molecules of water during its travel from anode to cathode. Since electro osmotic drag is completely dependent on the current density, membrane’s properties affect nothing on the phenomenon. Power to be produced for each fuel cell is determined by its size. Hence for every fuel cell a specified cut-in and cut-off value of current density. Excess current density floods and lower value dries up the anode electrode.

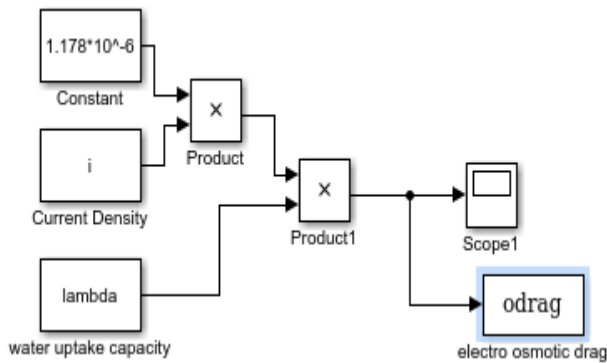


Fig 3: Simulink model for electro osmotic drag inside the fuel cell.

Temperature is an important criterion for the determination of performance of the fuel cell. Because the materials used in the fuel cell is directly dependent on temperature to determine the thermal stress developed inside the fuel cell. Continuous exposure of the membrane for long duration results in degradation of properties of membrane and its rupture. Hence a study is performed to determine the temperature distribution and calculate the thermal stress distribution and its effect on the working cycle of fuel cell for two different membranes.

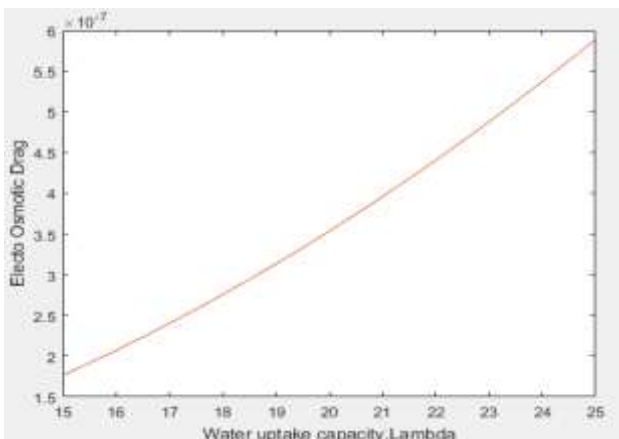


Fig 4: Graphical representation of electro osmotic drag.

Fig 5 represents the temperature distribution circuit blocks developed in Simulink. Analysis is conducted between room temperature and maximum working temperature of fuel cell i.e. 413K. The temperature distribution inside the fuel cell is a function of time, thermal and mechanical properties of the materials considered

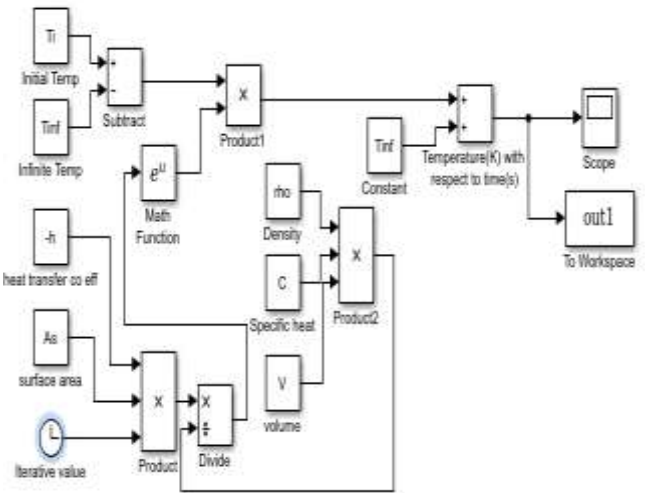


Fig 5: Simulink model for temperature difference.

Analysis is carried out along x-axis. The pressure maintained for working fluid is 1.5 Bar. Fig 6 and 7 reveals about the distribution of thermal stress for PTFE and Nafion membrane. The nature of graph for the two membranes is similar except the magnitude. With unit increase in reaction time, temperature increases by a factor of 10. After 40 seconds of reaction time, the reaction stabilizes and the graph shows linear behaviour. Compared to Nafion, PTFE experiences lower thermal stress because of its higher co-efficient of thermal expansion and Nafion has lower thermal conductivity compared to PTFE.

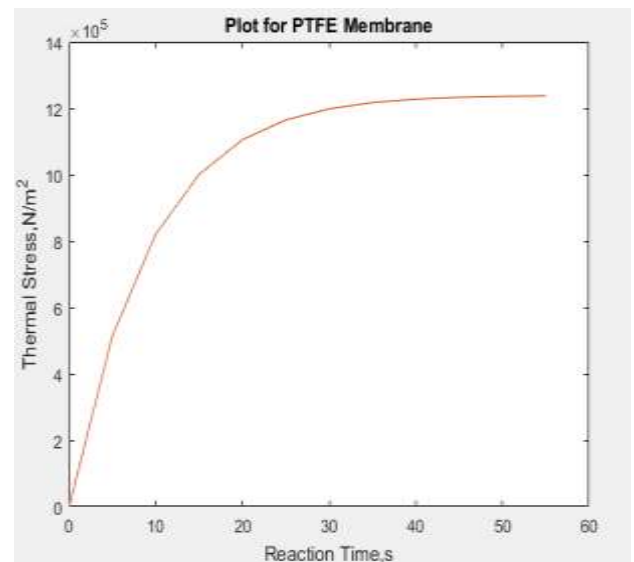


Fig 6: Plot for Thermal Stress Vs Reaction time for PTFE membrane

By studying the two graphs for thermal stresses, the value is low for PTFE compared to Nafion and the nature of plot is quite similar with respect to reaction time but co-efficient of thermal expansion for Nafion membrane is low. Thus PTFE expands more rapidly with per degree raise in temperature being pressure constant. Higher thermal conductivity is favorable because to dissipate the heat generated in the reaction chamber and thus number of cycles of operation for nafion is more compared to PTFE. Hence it is advisable to use Nafion membrane.

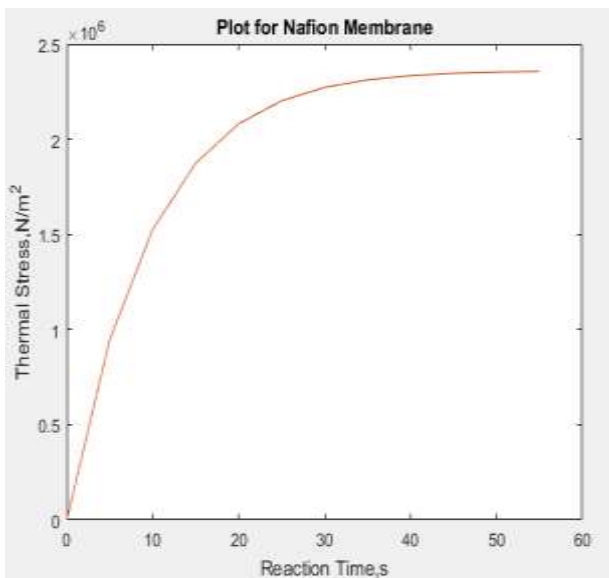


Fig 7: Plot for Thermal Stress Vs Reaction time for Nafion membrane

As reaction gets stabilized, temperature increases with respect to time. Concentration of water in anode, cathode and in flow channels plays a important role deciding the diffusion and back diffusion phenomenon and this process is depicted by diffusion co-efficient of water, which is dependent on water uptake capacity. The thickness of Nafion and PTFE membrane considered during simulation is 7 mils and 140 μ m respectively. Due to lower water content in anode, temperature and pressure is comparitvely higher than cathode side. Both diffusion and back diffusion increasas exponentially with respect to temperature and this is due to at mentioned working conditions with positive temperature raise causes effective water and proton transport.

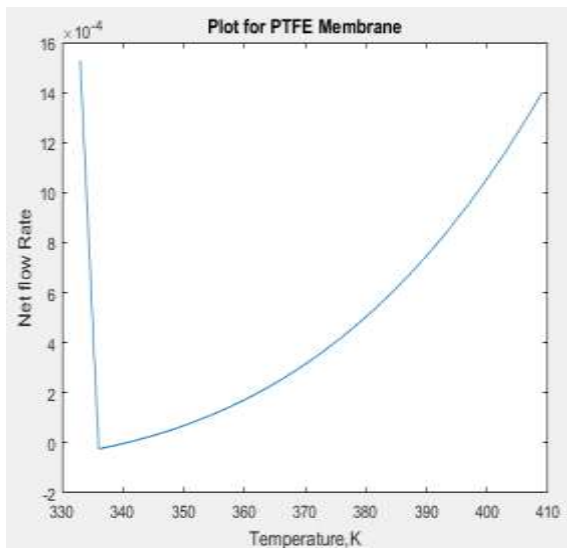


Fig 8: Graphical representation for PTFE membrane.

Net flow rate is the summation of electro osmotic drag, diffusion and back diffusion. After completion of each cycle, the net flow rate decreases to zero due to back diffusion. At the end of every stage, the concentration of water in cathode is more than that of anode. During the next cylce, as temperature increases, the rest water will flow from cathode to anode. After attaining equilibrium, the plot raises parabolically as shown in fig 8 and 9 indicating net flow rate increases by its square with respect to unit raise in temperature. With increase in temperature, flow of protons from anode to cathode resulting in the water trasport mechanism. For the PTFE membrane, fig 1.8 net flow rate magnitude is 16e-4 and for Nafion membrane is 14e-3.

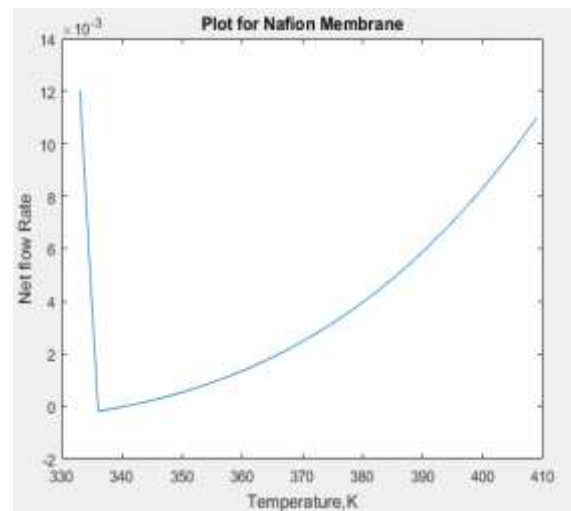


Fig 9: Graphical representation for Nafion membrane.

It is observed that for Nafion membrane 88 % net flow rate is more compared to PTFE membrane and this difference is due to thicknesses of membrane used, but this is positive to reduce the thermal stress developed in fuel cell. Water while transferring from anode to cathode, carry minor quantity of heat along it. It is advicable to use nafion as it permits maximum water transport percentage and this maintains the required humidity percentage also prevents drying of anode at high temperature operations.

5. Conclusions

Thermal stress distribution for Nafion and PTFE membrane, its effect on Proton and water transport for PEMFC is simulated using Matlab.

Positive change in the working temperature during fuel cell operation increases thermal stress exponentially.

Inspite of higher thermal stresses in Nafion compared to PTFE, Nafion allows net flow rate of water to be within the required limit of 13e⁻³. Exceeding this value causes flooding in fuel cell. Hence Nafion is best suited for PEMFC.

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Nomenclature

λ	Water uptake capacity
Φ	Ratio of pressure
N	Net flow rate of water, mol/sec
n_d	Humidification factor
I	Current density, A/m ²
F	Faradays Constant, 96485 C/mol
A	Surface area of membrane, m ²
D_w	Diffusion coefficient of water, m ² /sec
∂	Thickness, m
C	Concentration of fluid, mol/m ³
M	Molar weight, g
σ	Mean molecular radius of binary system, m
ρ	Density, kg/m ³
Ω	Dimensionless diffusion collision integral
EW	Equivalent weight

Subscripts and superscripts:

memb	Membrane used in fuel cell
eodg	Electro osmotic drag
bdn	Back diffusion
hpr	Pressure difference due to thermo osmosis
dif	Diffusion
an, cat	Anode and cathode area
(H ₂ - H ₂ O)	Hydrogen water binary system
(O ₂ – H ₂ O)	Oxygen water binary system
k	Knudsen diffusion
wc	Water concentration

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