ISSN: 2349-7300
ISO 9001:2008 Certified
International Journal of Innovative Research in Engineering & Multidisciplinary Physical Sciences (IJIRMPS)
Volume 2, Issue 2, April 2014

Use of finite element method as a simulation technique in the prediction of membrane resistance in Polymer electrolyte membrane for fuel cell operations

Andrew O. Odeh
Chemical Engineering Department, Vaal University of Technology
Vanderbijpark 1900, South Africa

Abstract: ***Fuel cells are posited to become alternate clean energy source of choice for the 21st century. The advantages of fuel cell are a high power output convenience for fuel supply and long life time. The heart of the fuel cell is the polymer membranes used as solid polymer electrolytes as it defines the properties needed for other components of the fuel cell. The efficiency and power density of the fuel cell strongly depend on the conductance of the polymeric material. The polymer membrane in a fuel cell functions twofold: it provides ionic communication between the electrodes as well as act as a separator for the fuel and oxidant. In this work, the finite element method (FEM) was applied to solve the second order derivative of Fick's law of diffusion in order to predict the resistance of the membrane to proton flow. Simulation results showed that the concentration of the desired fuel, in this case hydrogen increases at a fixed pressure with time. The theoretical predictions when compared with the actual experimental results showed an average deviation of 3.8%, an indication of a reasonable agreement between the model and the data from the experiment. Hence, the finite element method has been found to be satisfactory as a predictive tool to determine the resistance of membrane to proton transfer in any given membrane electrode assembly (MEA).***

Keywords: **Membrane, Resistance, Simulation, Fuel cells, Finite Element.**

I. INTRODUCTION

The quest for energy will continue to be an issue for mankind for the foreseeable future as long as procreation continues [1). Energy sources have been grouped under two broad categories: renewable and non-renewable. Fuel cells are considered as a tool for sustainable economic growth being a renewable energy source, high efficiency and its non-polluting effects. Fuel cells have also been identified as one of the most promising and potential clean energy technologies which meet all the requirements for energy security, economic growth and environmental sustainability, and have attracted considerable attention as a possible replacement for power generation systems [1]-[2]. Fuel cells have been noted to face many obstacles which researchers and industries must overcome before they can be widely introduced into the market place, one of these obstacles that must be overcome is the dire need to reduce the cost of the membrane and other components of the fuel cell, as well as the monopolization of membrane synthesis technologies by only a few companies and nations [3].

Among the different types of fuel cells, proton exchange membrane fuel cells (PEMFC) are now considered the best solution for automobile applications. This is due to the flexibility of their use and their low working temperature, which is important for the intrinsic safety of the vehicle [4]. Polymers are the materials more widely used for membrane manufacturing in virtue of their high processability, good intrinsic transport properties and low cost [5].The center of the fuel cell is the polymer membranes used as solid polymer electrolytes as it defines the properties needed by the other components of the fuel cell. The solid electrolyte use in fuel cell is a proton conducting material based on polymeric materials. The membrane material accounts for approximately 30 – 35% of the total cost of the fuel cell. Although many polymeric membranes have been developed, some with claimed superior performance, so far perflourinated sulphonic acid polymers produced and dominated by "dupont" represent the membrane material of choice for most membrane electrode assembly (MEA) manufacturers. This is basically because of their unique characteristics: it provides ionic communication between the electrodes, acts as an electronic insulator and a barrier to reactant crossover [6].

ISSN: 2349-7300
ISO 9001:2008 Certified
International Journal of Innovative Research in Engineering & Multidisciplinary Physical Sciences (IJIRMPS)
Volume 2, Issue 2, April 2014

Though the mechanism of proton is yet to be fully understood, the requirement that the membrane should be hydrated is crucial for optimum performance. Since the efficiency and power density of the fuel cell strongly depend on the conductance of the polymeric material, it implies that the selection of membrane material is crucial for the performance of the fuel cell. In order to cushion the expensive price monopoly by these few hands, alternative cheaper membrane materials has been developed and their membranes tested for performance in the fuel cell. Approaches such as: modifying the currently used commercial ionomer membranes to improve their properties, synthesizing new polymeric membranes and develop new polymer composites by blending the two polymers have been followed in the literature. In this study, the utilization of locally available material (i.e. Chitosan) in the synthesis of the membrane and its grafting with sulphonated zirconium oxide so as to improve its quality will contribute to the reduction in the cost of the fuel cell production and the improvement of its efficiency.

Mathematical modeling is an accepted scientific practice, providing the mechanism for comprehensively integrating basic processes and describing a system beyond what can be accomplished using subjective human judgments [3]. It is therefore possible to develop models that better represent the natural system and then use these models in an objective manner to provide a guide for current management practices, generate data, which hitherto have been limited for future research efforts. In this work, the finite element method (FEM) was employed to solve the second order differential of Fick's law of diffusion in order to test the composite membrane (chitosan-sulphonated zirconium oxide) produced in this study for resistance to proton flow [7]- [8]-[9].

II. THEORETICAL FRAMEWORK

The mass transfer is in the form of diffusion and by Fick's law of diffusion [10]:

$$\frac{\partial C_A}{\partial t} = D\frac{\partial^2 C_A}{\partial x^2} \tag{1}$$

Assumption 1: The flux is established across the membrane owing to the concentration gradients between the two adjacent components.
Assumption 2: The volumes of the adjacent compartments are larger the volume of the membrane and a pseudo-steady state will prevail before the concentration changes significantly. In other words, the flux across the membrane quickly reaches a pseudo steady state.
Assumption 3: The solutions are mixed well enough to prevent concentration gradients in each compartment.

A. Method of solution

Rearranging Eq. (1), we have:

$$0 = D\frac{\partial^2 C_A}{\partial x^2} - \frac{\partial C_A}{\partial t} \tag{2}$$

Developing the weak formulation of Eq. (2) by multiplying with the weight function, w

$$0 = w\left[D\frac{\partial^2 C_A}{\partial x^2} - \frac{\partial C_A}{\partial t}\right] \tag{3}$$

Integrating Eq. (3) over an element Ω^e

$$0 = \int_{x_e}^{x_{e+1}} w\left[D\frac{\partial^2 C_A}{\partial x^2} - \frac{\partial C_A}{\partial t}\right]dx \tag{4}$$

Applying methods of integration by parts,

$$0 = w\left[D\frac{dC_A}{dx}\right]\Bigg|_{x_e}^{x_{e+1}} - \int_{x_e}^{x_{e+1}} w\left[D\frac{dw}{dx}\frac{dC_A}{dx} + w\frac{dC_A}{dt}\right]dx \tag{5}$$

Let $x_e = x_a$ and $x_{e+1} = x_b$

$$0 = w\left[D\frac{dC_A}{dx}\right]\Bigg|_{x_b} - w\left[D\frac{dC_A}{dx}\right]\Bigg|_{x_a} - \int_{x_a}^{x_b} w\left[D\frac{dw}{dx}\frac{dC_A}{dx} + w\frac{dC_A}{dt}\right]dx \tag{6}$$

ISSN: 2349-7300
ISO 9001:2008 Certified
International Journal of Innovative Research in Engineering & Multidisciplinary Physical Sciences (IJIRMPS)
Volume 2, Issue 2, April 2014

Let $-Q_A = \left[D\frac{dC_A}{dx} \right]\Big|_{xa}$ and $Q_B = \left[D\frac{dC_A}{dx} \right]\Big|_{xb}$

This represents the value of the secondary variables at the boundary x_a and x_b respectively.

Then,

$$0 = \int_{x_a}^{x_b} \left(-D\frac{dw}{dx}\frac{dC_A}{dx} - w\frac{dC_A}{dt} \right) dx + w(x_b)Q(x_b) + w(x_a)Q(x_a) \tag{7}$$

Substituting $C_A \approx \sum_{j=1}^{n} C_{Aj}^e(t)\psi_j^e(t)$ and $w = \psi_i^e$

Eq. (7) becomes

$$0 = \int_{x_a}^{x_b} \left[-D\frac{d\psi_i^e}{dx}\left(\sum_{j=1}^{n} C_{Aj}^e(t)\frac{d\psi_j^e}{dx} \right) - \psi_i^e\left(\sum_{j=1}^{n} \psi_j^e \frac{dC_{Aj}^e(t)}{dt} \right) \right] dx + \sum \psi_i^e(x_j^e)Q_i^e \tag{8}$$

$$0 = \sum_{j=1}^{n} \int_{x_a}^{x_b} \left(-D\frac{d\psi_i^e}{dx}\frac{d\psi_j^e}{dx} \right) C_{Aj}^e(t)dx - \sum_{j=1}^{n} \int_{x_a}^{x_b} \left(\psi_i^e \psi_j^e \frac{dC_{Aj}^e(t)}{dt} \right) dx + \sum_{j=1}^{n} \psi_i^e(x_j^e)Q_i^e \tag{9}$$

The finite element model is represented as:

$$0 = [K_{ij}^e]\{C_{Aj}^e(t)\} - [M_{ij}^e]\left\{ \frac{dC_{Aj}^e(t)}{dt} \right\} + \{Q_i^e\} \tag{10}$$

But $\left[D\frac{dC_A}{dx} \right]_{x_A} = \left[D\frac{dC_A}{dx} \right]_{x_B} = 0$

Where

$[K_{ij}^e] = \int_0^{h_e} \left(-D\frac{d\psi_i^e}{dx}\frac{d\psi_j^e}{dx} \right) dx$, which is the stiffness matrix

$[M_{ij}^e] = \int_0^{h_e} \psi_i^e \psi_j^e dx$

Over the domain $\Omega^e = (0, h_e)$, where h_e is the height of the element.

For a quadratic element mesh

$$[K_{ij}^e] = \frac{D}{3h_e}\begin{bmatrix} -7 & 8 & -1 \\ 8 & -16 & 8 \\ -1 & 8 & -7 \end{bmatrix}$$

$$[M_{ij}^e] = \frac{h_e}{30}\begin{bmatrix} 4 & 2 & -1 \\ 2 & 16 & 2 \\ -1 & 2 & 4 \end{bmatrix}$$

For a mesh of two quadratic element, where $h_e = L$

$$[K] = \frac{D}{3L}\begin{bmatrix} -7 & 8 & -1 & 0 & 0 \\ 8 & -16 & 8 & 0 & 0 \\ -1 & 8 & -14 & 8 & -1 \\ 0 & 0 & 8 & -16 & 8 \\ 0 & 0 & -1 & 8 & -7 \end{bmatrix}$$

ISSN: 2349-7300
ISO 9001:2008 Certified
International Journal of Innovative Research in Engineering & Multidisciplinary Physical Sciences (IJIRMPS)
Volume 2, Issue 2, April 2014

But $\frac{D}{L} = k$

$$[K] = \frac{k}{3}\begin{bmatrix} -7 & 8 & -1 & 0 & 0 \\ 8 & -16 & 8 & 0 & 0 \\ -1 & 8 & -14 & 8 & -1 \\ 0 & 0 & 8 & -16 & 8 \\ 0 & 0 & -1 & 8 & -7 \end{bmatrix}$$

$$[M] = \frac{L}{30}\begin{bmatrix} 4 & 2 & -1 & 0 & 0 \\ 2 & 16 & 2 & 0 & 0 \\ -1 & 2 & 8 & 2 & -1 \\ 0 & 0 & 2 & 16 & 2 \\ 0 & 0 & -1 & 2 & 4 \end{bmatrix}$$

B. Time Approximated Solution

Since the concentration of A is time dependent, having developed the spatial approximation of the model, it is necessary to develop the time approximated solution of the finite element model (Eq. 10). The time approximated solution yields:

$$\left[\hat{K}\right]_{s+1}\{C_A\}_{s+1} = \left[\hat{K}\right]_s\{C_A\}_s + \{\hat{F}\}_{s+1}$$

Where,

$$\left[\hat{K}\right]_{s+1} = [M] + a_1[K]_{s+1}$$

$$\left[\hat{K}\right]_s = [M] - a_2[K]_s$$

$$\left[\hat{F}\right]_{s,s+1} = \Delta t_{s+1}\left[\alpha\{F\}_{s+1} + (1-\alpha)\{F\}_{s+1}\right]$$

But $\{F\}_{s+1} = \{F\}_s = 0$

$$a_1 = \alpha\Delta t_{s+1}$$

$$a_2 = (1-\alpha)\Delta t_{s+1}$$

Using $\alpha = 1$ (the backward difference scheme)

$$\left[\hat{K}\right]_1 = [M] + [K]_1 \qquad \left[\hat{K}\right]_0 = [M]$$

The finite element model becomes:

$$\{[M]\}\{C_A\}_s = \{[M] - \Delta t_{s+1}[K]\}\{C_A\}_{s+1} + \Delta t_{s+1}\{Q\}_{s+1} \tag{11}$$

$s = 0$, $\Delta t_1 = 600s$ and $\alpha = 1$

But $\{Q\}_1 = \begin{Bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{Bmatrix}$

Therefore, Eq. (11) becomes

$$\{[M]\}\{C_A\}_s = \{[M] - \Delta t_{s+1}[K]\}\{C_A\}_{s+1} \tag{12}$$

$$\{C_A\}_{s+1} = \{[M]\}\{C_A\}_s \bullet \{[M] - \Delta t_{s+1}[K]\}^{-1} \tag{13}$$

ISSN: 2349-7300
ISO 9001:2008 Certified
International Journal of Innovative Research in Engineering & Multidisciplinary Physical Sciences (IJIRMPS)
Volume 2, Issue 2, April 2014

The stiffness matrix and the mass matrix are evaluated respectively as given below:

$$K := \frac{k}{3}\begin{pmatrix} -7 & 8 & -1 & 0 & 0 \\ 8 & -16 & 8 & 0 & 0 \\ -1 & 8 & -14 & 8 & -1 \\ 0 & 0 & 8 & -16 & 8 \\ 0 & 0 & -1 & 8 & -7 \end{pmatrix} = \begin{pmatrix} -4.2\times 10^{-3} & 4.8\times 10^{-3} & -6\times 10^{-4} & 0 & 0 \\ 4.8\times 10^{-3} & -9.6\times 10^{-3} & 4.8\times 10^{-3} & 0 & 0 \\ -6\times 10^{-4} & 4.8\times 10^{-3} & -8.4\times 10^{-3} & 4.8\times 10^{-3} & -6\times 10^{-4} \\ 0 & 0 & 4.8\times 10^{-3} & -9.6\times 10^{-3} & 4.8\times 10^{-3} \\ 0 & 0 & -6\times 10^{-4} & 4.8\times 10^{-3} & -4.2\times 10^{-3} \end{pmatrix}$$

$$M := \frac{L}{30}\begin{pmatrix} 4 & 2 & -1 & 0 & 0 \\ 2 & 16 & 2 & 0 & 0 \\ -1 & 2 & 8 & 2 & -1 \\ 0 & 0 & 2 & 16 & 2 \\ 0 & 0 & -1 & 2 & 4 \end{pmatrix} = \begin{pmatrix} 2.667\times 10^{-3} & 1.333\times 10^{-3} & -6.667\times 10^{-4} & 0 & 0 \\ 1.333\times 10^{-3} & 0.011 & 1.333\times 10^{-3} & 0 & 0 \\ -6.667\times 10^{-4} & 1.333\times 10^{-3} & 5.333\times 10^{-3} & 1.333\times 10^{-3} & -6.667\times 10^{-4} \\ 0 & 0 & 1.333\times 10^{-3} & 0.011 & 1.333\times 10^{-3} \\ 0 & 0 & -6.667\times 10^{-4} & 1.333\times 10^{-3} & 2.667\times 10^{-3} \end{pmatrix}$$

C. MathCAD Simulation of finite element solution

MathCAD was used to simulate the time dependent concentration distribution of the solution across the membrane surface. The simulation was possible by incorporating the finite element solution into the MathCAD software (Chapra and Canale, 2006).

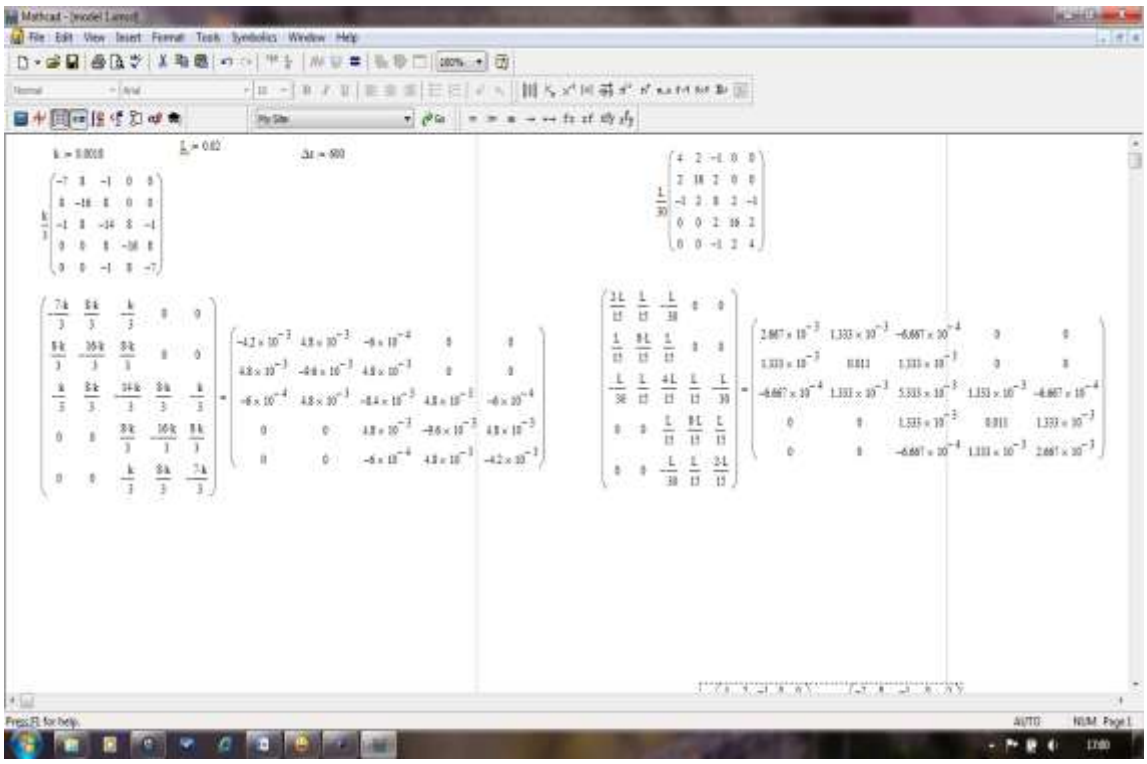

Fig. 1: Mathcad interface of the solution of the stiffness matrix

ISSN: 2349-7300
ISO 9001:2008 Certified
International Journal of Innovative Research in Engineering & Multidisciplinary Physical Sciences (IJIRMPS)
Volume 2, Issue 2, April 2014

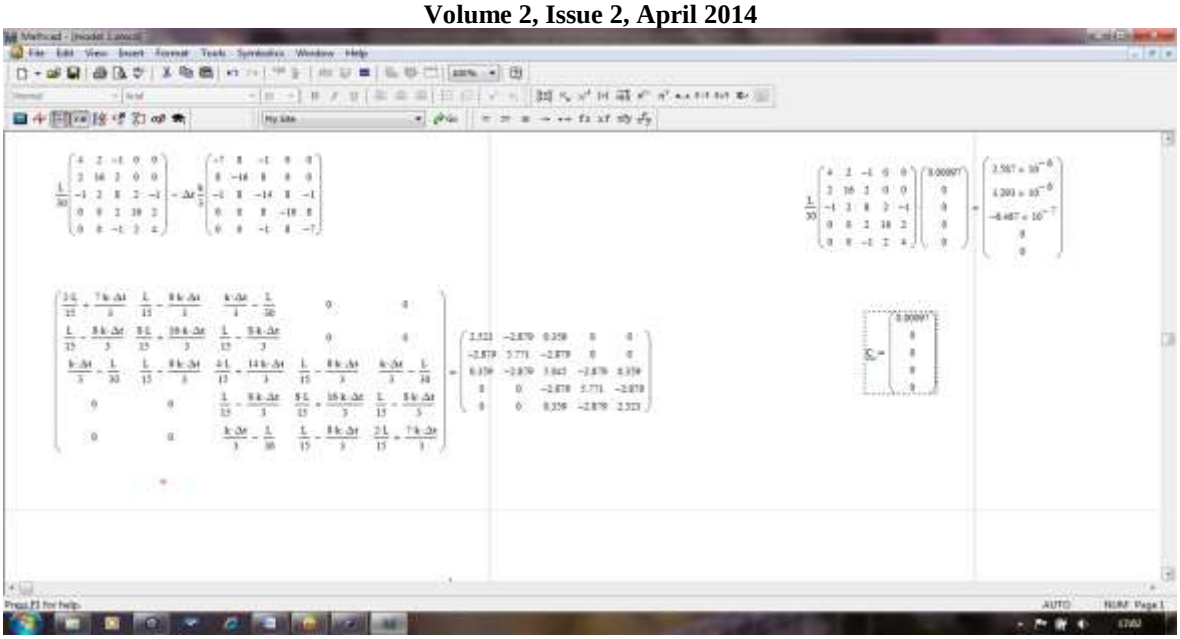

Fig. 2: Mathcad interface of the solution of the stiffness matrix

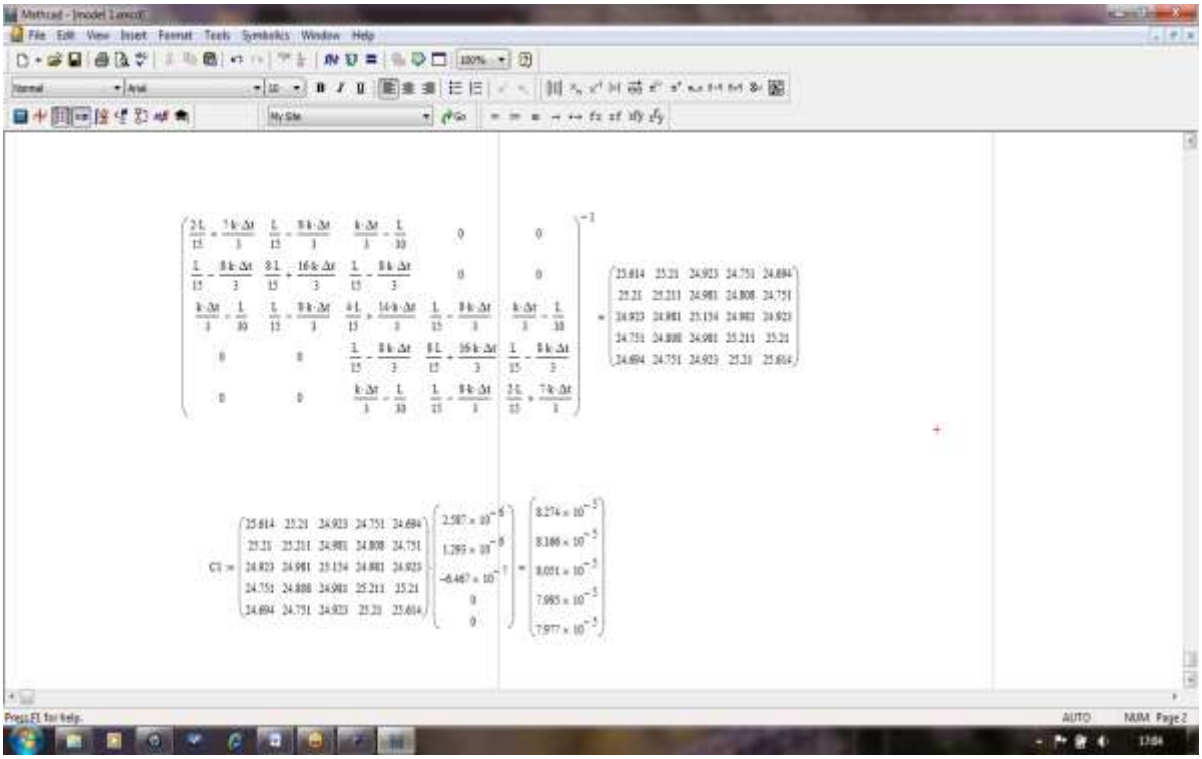

Fig. 3: Mathcad interface of the simulated result

III. RESULTS AND DISCUSSION

The results of the computation analysis of the modeling equation for the resistance of membrane to proton flow using the finite element simulation technique are illustrated below. The model was applied to simulate the concentrations of the proton ion (hydrogen) that passed through the composite membrane prepared from chitosan and sulphonated zirconium oxide.

ISSN: 2349-7300
ISO 9001:2008 Certified
International Journal of Innovative Research in Engineering & Multidisciplinary Physical Sciences (IJIRMPS)
Volume 2, Issue 2, April 2014

Figure 4 and 5 show the variation of the computed permeability from the concentration of hydrogen ion with time. The profile revealed that the membrane will perform better when it is fully hydrated rather than partially hydrated membrane. It was also observed that the thinnest membrane will produce the lowest internal resistance, but the thickness must be high enough to slow the molecular diffusion of the fuel gases and ensure that the membrane is strong enough for fuel cell applications. Otherwise, the results would be poor current density and waste of fuel gas by diffusion, especially during long running period.

The developed model which had a number of variables whose numerical values were independently estimated was validated to assess the variation of the simulated composition of the proton flow through the membrane with time. A comparison of the experimental and simulated result is shown in Figure 5. Generally, the numerical solution of the model proton flow through the membrane gave a reasonable agreement with the experimental data with an average deviation of 3.8%.

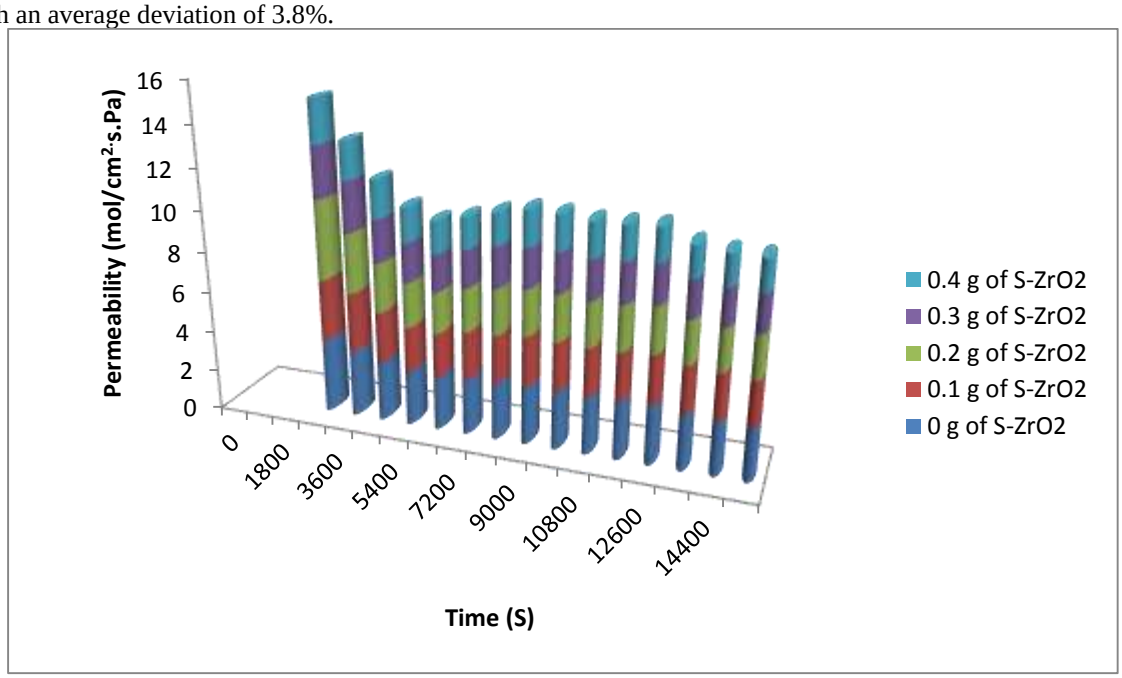

Fig.4: Variation of permeability of proton with time

ISSN: 2349-7300
ISO 9001:2008 Certified
International Journal of Innovative Research in Engineering & Multidisciplinary Physical Sciences (IJIRMPS)
Volume 2, Issue 2, April 2014

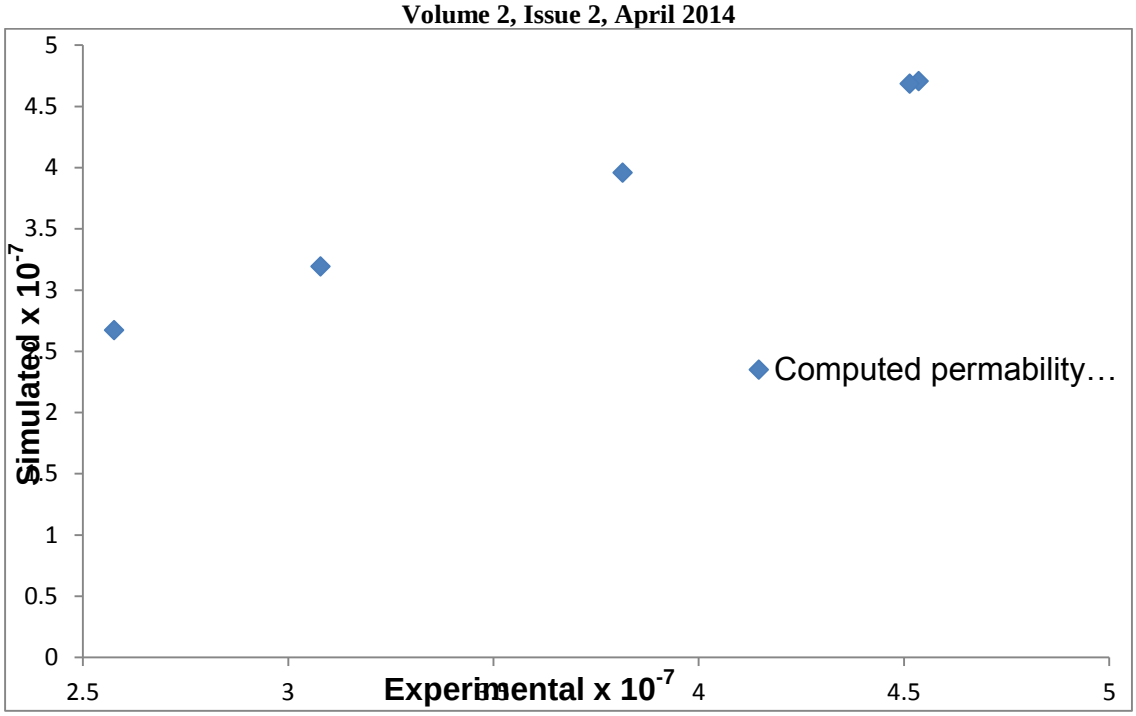

Fig. 5: Experimental and simulated permeability of proton across the membrane

IV. CONCLUSION

The finite element method has been an established numerical method of solving partial differential equations, integrating it with the Fick' s equation for diffusion is seen as a novel approach in characterizing membranes for fuel cells. In this study, the finite element method has been found to be satisfactory in solving the Fick's law of diffusion with regards the second derivative and can be used to predict the concentration gradient between cathode and anode ends in a membrane electrode assembly. This therefore does not necessitate the need for experimental assay for the search for membrane to be used in fuel cell operations.

This model can also be used to determine the actual flow of protons across the membrane in the membrane electron assembly.

REFERENCES

[1] A.O Odeh, P.O. Osifo, and H.W.J.P. Neomagus, "Progress in Polymer Electrolyte Membrane Research for Fuel Cell Applications - The Issue of Water Management," Lecture Notes in Information Technology, vol.13: pp.15 – 22, 2012.

[2] K Sopian, and R.W. Wan Daud, "Challenges and future developments in Proton exchange membrane fuel cells," Renewable Energy, vol. 35, pp. 719- 729, 2006.

[3] Y.Zhou, "Assembly and Performance modeling of Proton Exchange Membrane Fuel Cells", PhD thesis submitted to University of Michigan, USA, 2009.

[4] J.G. Pharoah, "On the permeability of gas diffusion media used in PEM Fuel Cells", Journal of Power Sources, vol.141, pp. 47 – 64, 2005.

[5] A.M. Hichner, "Transport and Structure in Fuel Cell Proton Exchange Membranes", PhD thesis submitted to Virginia Polytechnic Institute and State University, USA, 2003.

[6] G.H. Guvelioglu, and H.G. Stenger, "Computational fluid dynamics modeling of polymer electrolyte membrane fuel cells," Journal of Power Sources, vol.147, pp.95 – 106, 2005.

[7] S.C. Chapra, and R.P. Canale, "Numerical Methods for Engineers", 5th edition. New-York: McGraw-Hill Inc., 2006.

[8] C.S. Desai, and J.F. Abel, "Introduction to the Finite Element Method: A numerical method for Engineering Analysis", New-York: Van Nostrand, 1972.

ISSN: 2349-7300
ISO 9001:2008 Certified
International Journal of Innovative Research in Engineering & Multidisciplinary Physical Sciences (IJIRMPS)
Volume 2, Issue 2, April 2014

[9] J.N. Reddy, "An Introduction to the Finite Element Method," Second Edition. New-York: McGraw-Hill Inc., 1993.

[10] R.B. Bird, W.E. Stewart, and E.N. Lightfoot, "Transport Phenomena", New- York: Wiley. 1960.