Modeling the Behaviour of a Polymer Electrolyte Membrane within a Fuel Cell Using COMSOL

S. Beharry[1]
[1]University of the West Indies, St. Augustine, Trinidad and Tobago

Abstract: In recent years, scientists have taken great interest in the development of renewable and alternative energy sources. One viable alternative to non-renewable fossil fuels is the fuel cell, which produces electricity via a simple chemical reaction using hydrogen and oxygen gases with little or no pollution as the only by-products formed are heat and water. A special class of FC i.e. Proton Exchange Membrane Fuel Cell (PEMFC) has been investigated during the present study. Membrane is a very important part of a PEMFC as most ohmic losses occurs here and limits the maximum operating temperature, causes fuel cross over effect and increase electrochemical kinetics losses resulting in reduced fuel efficiency and cathode catalyst poisoning. Therefore there is a need of an accurate modeling of the membranes to study the overall physical and electrical behaviour of real Fuel Cells. In this project Poly (1-vinylimidazole) or PVIm polymer membrane has been modeled and its performance has been investigated by studying its conductivity, heat flow and weight loss at various temperatures and compositions. Modeling has been done using simulation software, COMSOL Multiphysics 4.2a, which allows the application of various physics interfaces to the model and facilitates all the necessary steps needed to ensure that the model is as realistic as possible.

Keywords: Proton Exchange Membrane Fuel Cell (PEMFC), Poly (1-vinylimidazole) or PVIm polymer membrane, Fuel cell modeling.

1. Introduction

Scientists have deemed the fuel cell as one of the most promising power sources that can replace the use of fossil fuels as well as satisfy global expectations. The PEM fuel cell shows great potential to power houses and vehicles. The membrane of the PEMFC is one of the most fundamental parts of the cell as its properties have great impact on the cell's output capability. Most PEMFCs employ the use of hydrated membranes. This proposes a problem where the membrane only works properly at temperatures below 80°C, because above this, the water in the membrane would start to evaporate leading to membrane degradation and lowering the cell's output voltage. The Poly(1-vinylimidazole) (PVIm) polymer is a material which is used and does not involve the presence of water for operation as a membrane. The PVIm material was developed by research students at the Fuel Cell Materials Research Laboratory in the Department of Physics at the University of the West Indies (UWI) [1]. This polymer, when combined with triflic acid forms an acid-base ternary composite blend based membrane. The acid-base interaction within the membrane as well as the addition of nano-composite materials leads to increased proton conductivity and morphology which results in larger output voltages. In this particular membrane, nano-tubular titania are included in the base polymer matrix. The membrane also has high chemical, thermal and mechanical stability making it suitable for use in a PEMFC for temperatures much greater than 80°C.

In this project, a model of the PVIm polymer membrane was made. This model was applied to different compositions of the acid-base blended membrane with special attention to the composition of PVIm-Triflic acid- PVDF-HFP in the ratio of 5-2-3. The modeling process was done using COMSOL Multiphysics 4.2a.

2. PEMFC model development

2.1 Structural model

A computational domain was created as well as a computational mesh as seen in Fig. 1 and Fig. 2 respectively. There are two separate gas channels at the anode and cathode which allows for hydrogen and oxygen gases to enter the fuel cell. The channels are bounded by graphite sheet bipolar plates which are highly conductive, both thermally and electrically and are also stable at high temperatures. Between the two channels is the membrane electrode assembly (MEA). The

MEA comprises two carbon fibre gas diffusion layers (GDLs) which allow the incoming gases to be dispersed throughout the entire reaction surface layers. Hence there are also two reaction layers which are made of platinum where the gases undergo the following chemical reactions:

At anode:
$2H_2 => 4H^+ + 4e^-$

At cathode:
$O_2 + 4H^+ + 4e^- => 2H_2O$
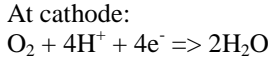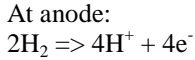
The last component of the MEA is the PVIm membrane. The membrane allows protons to flow within the cell, from the anode to the cathode. The membrane thickness is $\pm542\cdot10^{-6}$ [m].
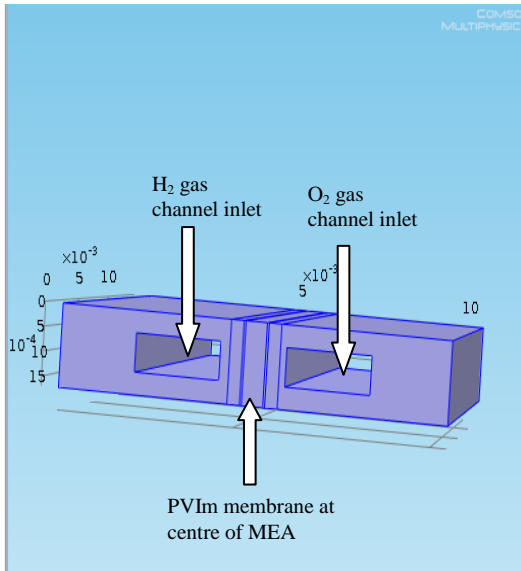

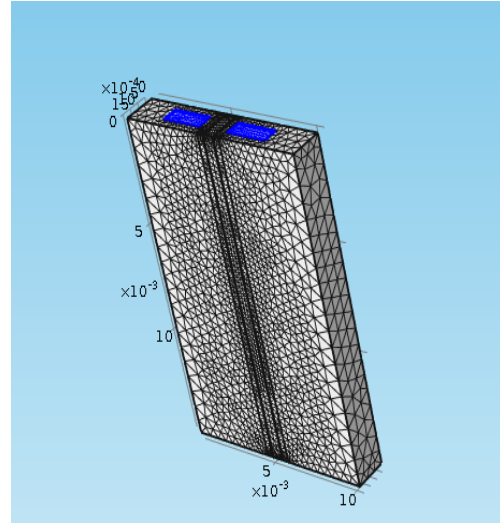**Figure 1**. Computational domain showing gas channels and MEA present within the structure.

Figure 2. Computational mesh.

2.2 Assumptions

In order to develop the model, several assumptions were made [2]. The fuel cell operates under time-dependant conditions. No water passes through the membrane. Flow of gases is laminar in all channels. The gas inlet conditions are fully developed. All gases are ideal. Gases do not cross over into other channels. Since the fuel cell operates at temperatures higher than $80^{\circ}C$, there is single-phase water flow. All electrochemical reactions occur in the gaseous phase. The parameters of the materials used in the model are homogenous and isotropic.

2.3 Governing Equations

The physical operations within the model for its successful simulation were accomplished using COMSOL Multiphysics 4.2a. Several different mathematical parameters had to be applied and solved.

For multi-component gas diffusion, the Maxwell-Stefan diffusion model was used:

$$\rho\frac{\partial}{\partial t}(\omega_i) + \rho(\mathbf{u}\cdot\nabla)\omega_i = \nabla\cdot\left(\rho\omega_i\sum_{k=1}^{Q}\tilde{D}_{ik}\mathbf{d}_k + D_i^T\frac{\nabla T}{T}\right) + R_i$$

where ωi = mass fraction; ρ = density; R_i = rate expression; u= velocity of mixture; $\check{D}_{ik}$ = multicomponent Fick diffusivities; d_k= diffusional driving force; D_i^T = thermal diffusion coefficient.

Fluid flow in porous media is governed by the Brinkman equation:

$$\frac{\rho}{\varepsilon_p}\left(\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla)\frac{\mathbf{u}}{\varepsilon_p}\right) =$$

$$-\nabla p + \nabla \cdot \left[\frac{1}{\varepsilon_p}\left\{\mu(\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3}\mu(\nabla \cdot \mathbf{u})\mathbf{I}\right\}\right] - \left(\frac{\mu}{\kappa} + Q_{br}\right)\mathbf{u} + \mathbf{F}$$

where μ= dynamic viscosity of the fluid; u= velocity; ρ= density of the fluid; p= pressure; ε_p= porosity; κ= permeability of the porous medium; Q_{br} = a mass source or mass sink; influence of gravity and other volume forces can be accounted for via the force term F.

The following equation was used to describe the heat transfer in the porous media:

$$(\rho C_p)\, \partial T/\partial t + \rho C_p u \cdot \nabla T = \nabla \cdot (k_{eq} \nabla T) + Q$$

where ρ is the fluid density; C_p is the fluid heat capacity at constant pressure; k_{eq} is the equivalent thermal conductivity; u is the fluid velocity field; Q is the heat source (or sink).

The equivalent thermal conductivity is:

$$k_{eq} = \Theta_p k_p + \Theta_L k_L$$

where Θ= volume fraction; the subscripts p and L represents the solid and the fluid respectively.

Therefore it can be seen that $\Theta_p + \Theta_L = 1$.

2.4 PVIm membrane

The membrane used is made of a material called Poly (1-vinylimidazole). The compound shown in Fig. 3 is the monomer unit for the PVIm polymer [3]. This compound is repeated within the polymer's structure. The 'N' highlighted in red is the nitrogen which is responsible for the PVIm being able to act as a proton transfer mechanism. This nitrogen has a lone pair of electrons which can form a bond with a proton. This bond leaves the nitrogen with a net positive charge, but this is stabilized via the adjacent pi electrons within the ring arrangement. This chemical formula had to be obtained and used in order to add the PVIm material into the COMSOL simulation.
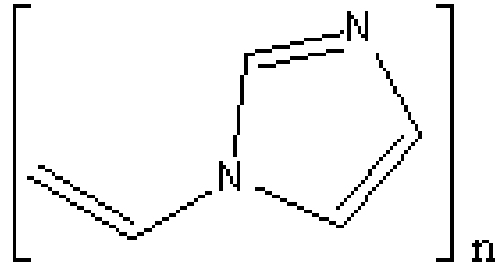

Figure 3. Chemical structure of PVIm compound

The development of the Poly(1-vinylimidazole) based membrane was done by Ms. Kerrilee Stewart and Dr. H.P.S. Missan in the Fuel Cell Materials Research Laboratory in the Physics department at UWI. The PVIm compound was combined with triflic acid so as to establish acid-base interactions and create a ternary membrane. Acid-base membranes have increased proton transport ability thereby increasing the proton conductivity and the output voltage. A stable hydrophobic backbone was created for the membrane with the inclusion of PVDF-HFP (polyvinylidene fluoride-co-hexafluoropropene). This polymer belongs to the group of thermoplastics and has high chemical, thermal and mechanical stability. The conductivity and morphology as well as thermal stability of the membrane were further increased through the addition of nano-tubular titania within the membrane matrix.

Conductivity measurements were obtained for different compositions of PVDF-HFP-Triflic acid-PVIM for the membrane respectively. The 5-2-3 membrane with 2%wt. titania showed the highest conductivity [1]. The thermal conductivity and heat capacity of the PVIm based membrane were calculated from DSC and thermogravimetry (TGA) studies performed on the membrane.

2.5 Boundary Conditions

The experimental development of the fuel cell required special boundary conditions to be

specified. Thermal insulation boundaries were used for internal boundary conditions. For the gas channels, temperature, pressure, flow rate and composition were applied. The voltage and temperature of the cell based on the membrane operation were applied at the bipolar plates.

3. Results

The highest conductivity obtained using the PVIm membrane was 3.542×10^{-2} S/cm at 60°C for the 5-2-3 composition with 2%wt [1]. Modeling was done based on this composite membrane. The free and porous media flow within the model was examined as seen in Fig. 4. The densities of the gases entering the channels lead to the results shown. Hydrogen is the less dense than oxygen and therefore has a faster flow rate.
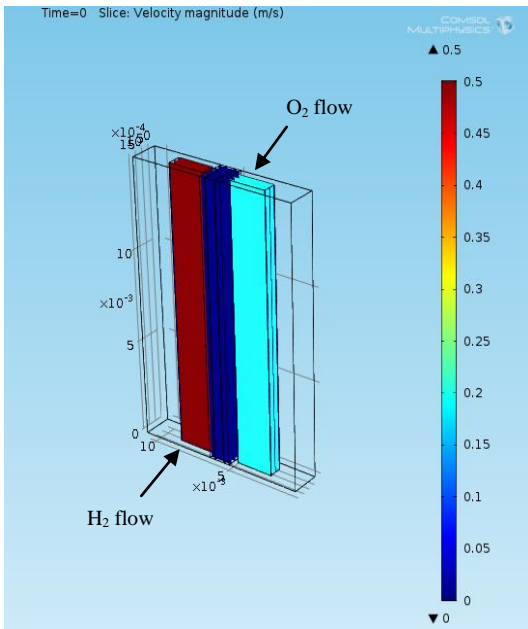

Figure 4. Porous media flow within channels

The secondary current distribution was then obtained as seen in Fig. 5 and Fig. 6 across the membrane. The voltage is significantly increased from the anodic side of the cell model to the cathodic side as protons flow through the membrane to give a maximum output of 0.95V.
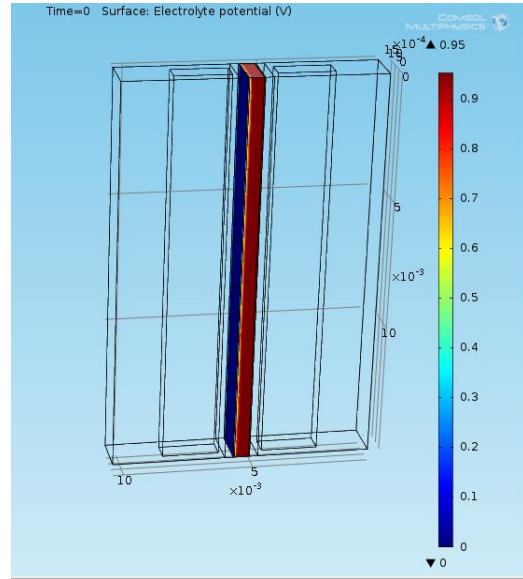

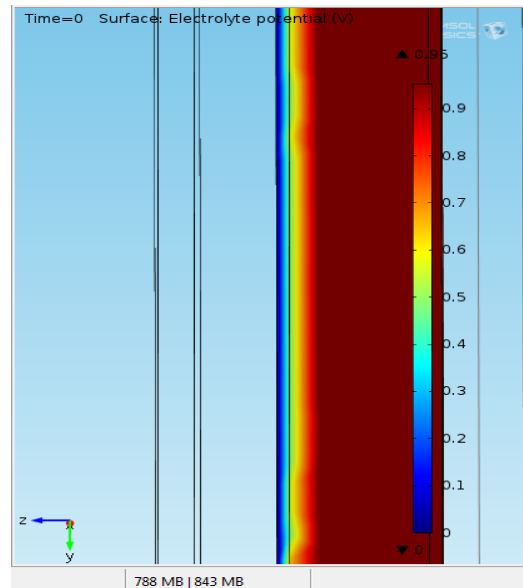**Figure 5**. Secondary current distribution in the PVIm membrane

Figure 6. Magnified view of the membrane

The cold gas entering the cell may cause cooling of the membrane. This can lead to a lowering of proton conductivity causing higher ohmic losses within the cell.

4. Conclusions

A three-dimensional model of a PEMFC using a PVIm membrane was created. It was noted that the density of the gases entering the cell affects the rate of flow across the GDLs. Also, the temperature of the inlet gases can cause a lessening of proton conductivity and increased ohmic losses. This model shows fairly good agreement with experimental values. However, further studies are necessary in order to validate the use of the PVIm material as a viable high-temperature membrane.

5. References

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6. Acknowledgements