

Modeling Proton Transport in Hydrophobic Polymeric Electrolytes

M. Andrews¹, H.P.S. Missan^{*1}, D. Sharma¹

¹University of the West Indies, St. Augustine Campus, Trinidad, West Indies

*harrinder.missan@sta.uwi.edu

Abstract: The Polymer Electrolyte Membrane fuel cell is one of the most promising green technologies for addressing portable, as well as transportation power needs. However, the science behind the fuel cell, in many regards, is still an enigma, and even more so, with the vast numbers of novel materials created annually; designed to offset issues related to durability, conductivity, cost-effectiveness and manufacturability of fuel cell components. This paper presents a computational model in COMSOL that shows the rate of proton transport in a novel hydrophobic polymer electrolyte and is based on a two phase hydraulic membrane. The model provides its user with a visual approach for assessing a polyelectrolyte based on its microstructure and also provides insight into potential mechanisms of species transport within the material.

Keywords: fuel-cell, polymer-electrolyte, proton-transport, COMSOL, modeling.

1. Introduction

A fuel cell is an electrochemical energy generating device. As an electrochemical device, the fuel cell shares many similarities, in terms of its principles of operation, with other electrochemical systems, and more specifically, batteries. Some of these properties include:

1. The thermodynamic and kinetic principles
2. An exothermic red-ox pair of chemical reagents
3. An anode and cathode - which facilitate catalytic processes such as electron liberation and conduction as well as lowering activation energy of reagent molecules
4. An electrolyte, which provides spatial separation of the reagents, insulation of the liberated electrons and transport of ions between electrodes - thereby completing the electrical circuit

5. And electrical losses due to the resistive properties of the electron and ion transport media

Unlike typical batteries, which store a finite amount of electrical energy in the form of chemical energy, the ideal fuel cell produces electricity once it is supplied with reagents, and, as such, is analogous to a power generation plant. In addition, combinations of exothermic red-ox pairs can be selected to have little or no greenhouse gas emissions thereby facilitating the use of sustainable fuels such as Hydrogen or Biofuels.

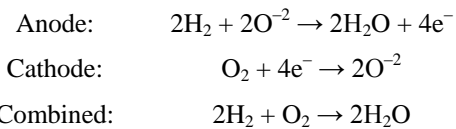


Table 1: Electrochemical reactions of a Hydrogen Polymer Electrolyte Fuel Cell (HPEMFC)

The past four decades have seen several improvements in terms of materials (catalysts and membrane-electrode assemblies), fabrication techniques, and system designs, but these are still dwarfed by limitations in the development of durable and affordable super ionic conducting electrolytes (*like* Nafion[®] but cheaper). In fact, solid state electrolytes have played a minimal role in improving fuel cell technology to-date. This is mainly due to limitations in understanding of the transport phenomenon occurring in polymer electrolytes.

This paper demonstrates a two dimensional computational model that shows the rate of transport of a fluid through a porous hydrophobic material. COMSOL was used to determine the velocities and pressures of this fluid within the membrane.

2. Polymer Electrolytes

The existing literature on super ionic conductors (SIC's) has proposed that proton conduction in solid electrolytes occurs primarily

through a Grotthus-type or ion hopping mechanism. This is dependent on the concentration of H^+ ions entering the membrane and the availability of suitable pathways that would lead to complete traversal of the membrane.

In the case of water dependent membranes, such as Nafion[®], (Schmidt-Rohr & Chen 2008) proposed a tri-phase tubular model, consisting of an outer flexible polymer backbone, a water trapping layer - resulting from the negatively charged sulfonate groups and an osmotically driven water channel. This combination of characteristics facilitates the transport of protons by ion - hopping as well as the movement of the water present in the membrane.

Heterocyclic or “dry” proton conducting membranes typically contain imidazole, pyrazole or benzimidazole in place of the hydrophylic benzyl sulphonic groups that exist in water dependent polyelectrolytes. Heterocyclic groups replace water as the proton transporter (Kreuer et. al. 1998). This suggests that the aforementioned SIC's consist of two phases - the polymer backbone, and the mobile functional groups. (Kreuer et. al. 2001) proposed the kinetics of this reaction.

2.1 Hydrated Membrane Analogy

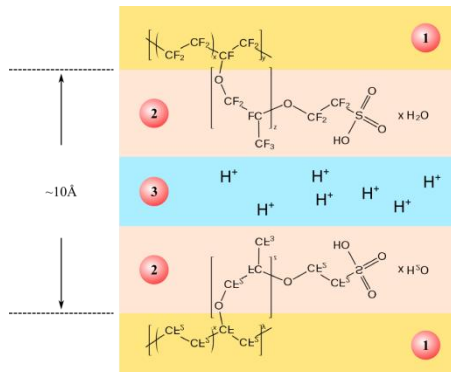


Figure 1. A pore of a water dependent polyelectrolyte

The above diagram presents a visual representation of a conducting pore in a Nafion-type membrane. The pore is assumed to have an internal diameter of 10Å.

Region 1 of figure 1, represents the no-flow section of the model and is assumed to consist of a perfectly elastic, impervious layer. H^+ concentration, velocity and pressure are all assumed to be zero. Region 2 consists of a

hydrophilic, proton-rich, porous layer. Protons are exchanged between this section and region 3 via concentration-driven diffusion. Region 3, being a nano-scaled pore, is assumed to exhibit laminar fluid flow.

2.2 Dry Membrane Analogy

The dry membrane consists of the polymer backbone as well as the self diffusing heterocyclic groups. As such, the membrane is considered to participate in the transport of protons from the anode to cathode. (Kreuer et. al. 2001).

3. Methodology

Novel hydrophobic membranes have been studied at the University of the West Indies' Fuel Cell Research Laboratory. Morphological and dimensional studies, for several polyvinylidene fluoride vinylimidazole-based polymers using scanning electron microscopy (SEM), were conducted and documented (Stewart, Singh, and Missan 2009). The SEM image for Poly(vinylidene fluoride)-graft-vinylimidazole (PVDF-g-Vim), referred to as membrane A, was converted into a .dxf file using the open source application Inkscape, and this vectorized image was imported into COMSOL for processing.

4. Use of COMSOL Multiphysics

(Colomban 1992) proposed that ionic transport in polyelectrolytes occurs in materials that possess both amorphous and crystalline states. The crystalline states are static while the amorphous are dynamic. The dynamic paths, also referred to as pores, and were assumed to have characteristics similar to water vapor, in the first instance. Table 1 below shows the parameters employed.

Parameter Name	Value/ Units	Description
P_init	1.01325e5 [pa]	Initial pressure
rho_vapour	0.6[kg/m ³]	Density of steam
rho_polymer	2.05e3[kg/cm ³]	Density of polymer
neta_vapour	1e-5[pa*s]	Viscosity of steam
neta_polymer	40[pa*s]	Viscosity of polymer

Table 1. Modeling parameters of steam-like dynamic phases

In the second case the pores were assumed to have characteristics similar to those of the Poly(vinylidene fluoride)-graft-vinylimidazole. The dynamic phase was assumed to possess a density and dynamic viscosity of ¼ that of the crystalline phase. In addition, the movement of the fluid through the membrane was assumed to be based on single phase, laminar, pressure driven flow – due to the small sizes of the pores (~2nm). Table 2 bears the parameters used for the second model.

Parameter Name	Value/ Units	Description
P_init	1.01325e5 [pa]	Initial pressure
rho_polymer	2.05e3[kg/cm ³]	Density of polymer
neta_polymer	40[pa*s]	Viscosity of polymer
rho_vapour	rho_polymer* 0.25	Density of vapour
neta_vapour	neta_polymer* 0.25	Viscosity of vapour

Table 2. Modeling parameters of polymer-like dynamic phases

The model employs the Laminar flow interface of COMSOL. Due to the small width of the membrane, <10 µm, and the rate of transport of matter in the amorphous phases, the time intervals under which the flow occurs are considered to be infinitesimal. As such, the model is steady state.

The partial differential equations for the Laminar flow interface are as follow:

Boundary & initial conditions:

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \quad \dots 1$$

$$p = 0 \quad \dots 2$$

Partial differential equations (2 dimensional Cartesian):

$$\frac{\partial u}{\partial t} + \frac{\partial u}{\partial x} + \frac{\partial u}{\partial y} = -\frac{1}{\rho} \frac{\partial p}{\partial x} + \mu \left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right) \quad \dots 3$$

$$\frac{\partial v}{\partial t} + \frac{\partial v}{\partial x} + \frac{\partial v}{\partial y} = -\frac{1}{\rho} \frac{\partial p}{\partial y} + \mu \left(\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} \right) \quad \dots 4$$

$$p = P_init \times \text{ramp}() \quad \dots 5$$

$$\frac{\partial u}{\partial t} = \frac{\partial v}{\partial t} = 0 \quad \dots 6$$

Equations 3 and 4 represent the Cartesian form of the Navier-Stokes equation. The symbols are defined as follows: u and v are the velocities of the fluid along the x and y axes, μ and ρ are the viscosity and density of a given fluid. Note, that the gravitational effects of the fluid within the membrane are assumed to be insignificant; $\text{ramp}()$ is a linear range function implemented in COMSOL. Its initial value is 0, its gradient is 1 and its maximum value is 10. It was implemented to simulate a gradual increase in pressure at the membrane inlet.

Figure 2 represents the SEM image of the polyvinylidene fluoride vinylimidazole polymer. The black region is the amorphous phase of the polymer and the grey - the crystalline. The red border represents the interface between the two phases. The sample size investigated was approximately 2.2µm×1.5 µm.



Figure 2. Vectorized version of membrane A

5. Figures

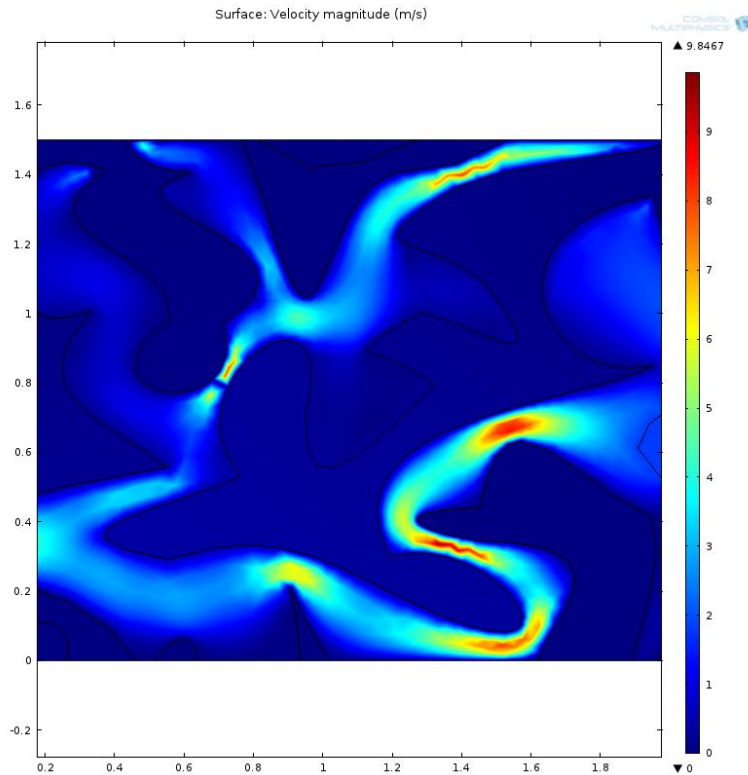


Figure 3. Velocity profile of steam-like amorphous phase of Poly(vinylidene fluoride)-graft-vinylimidazole

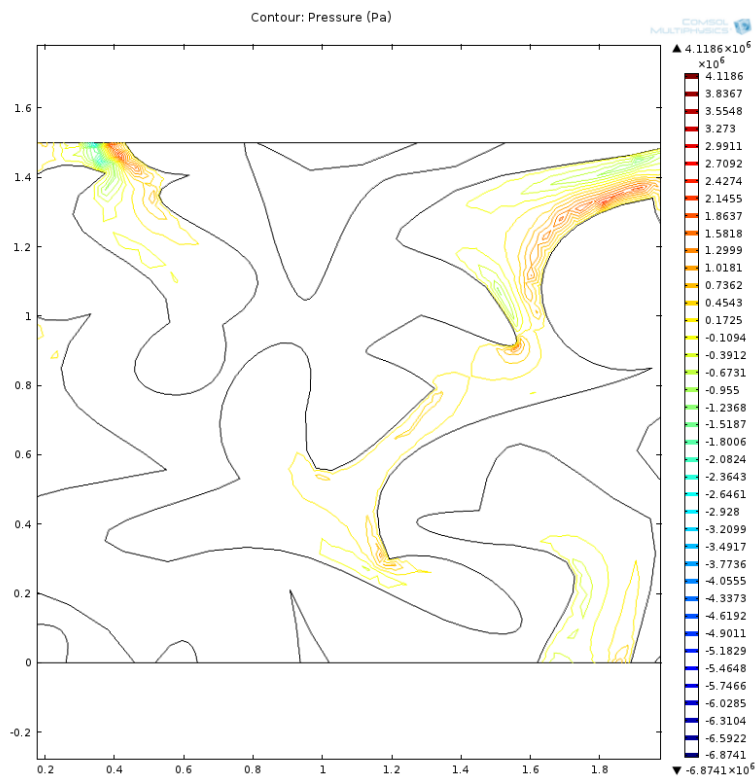


Figure 4. Pressure profile of steam-like amorphous phase of Poly(vinylidene fluoride)-graft-vinylimidazole

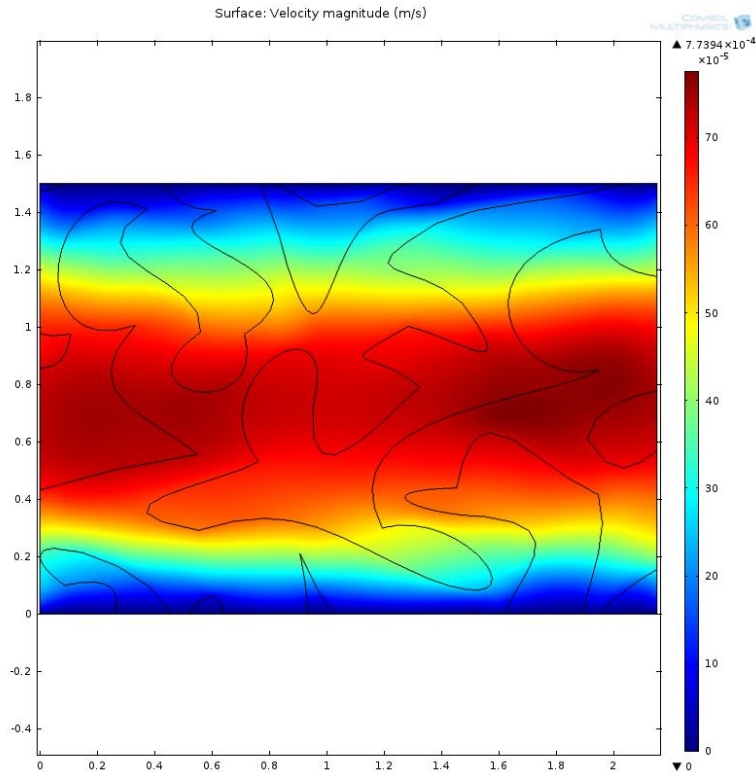


Figure 5. Velocity profile of polymer-like amorphous phase of Poly(vinylidene fluoride)-graft-vinylimidazole

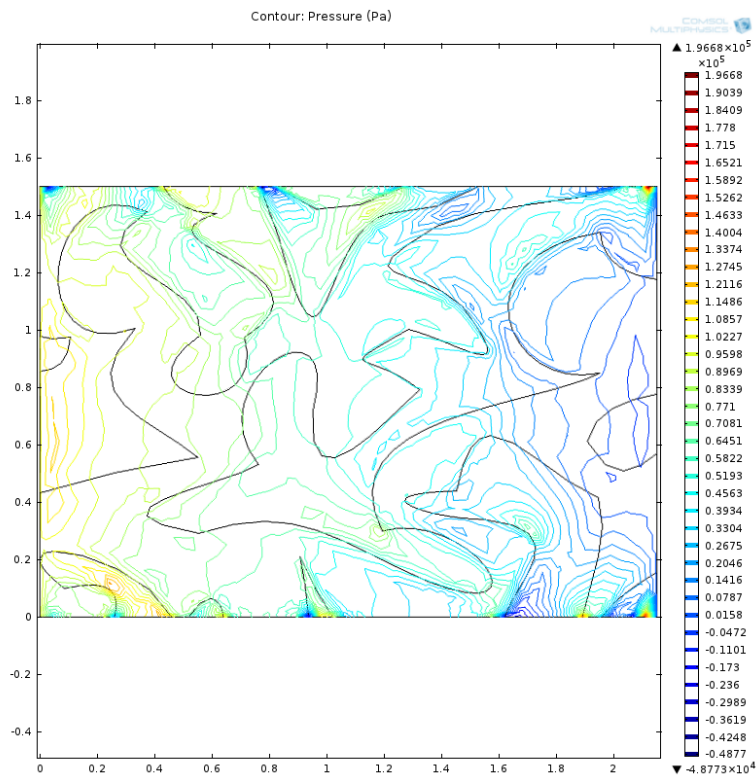


Figure 6. Pressure profile of polymer-like amorphous phase of Poly(vinylidene fluoride)-graft-vinylimidazole

COMSOL was utilized to add another layer of understanding to the material research. The mechanism of transport of reagents in polymer electrolytes is currently unknown. However, the dynamic phase which is ultimately responsible for proton transport may consist of protonated water vapour or protons sheathed by mobile polymer fragments. Most researchers focus primarily on the current density or impedance of the membrane as these provide data for modeling fuel cell systems, however, these properties do not enable a materials scientist or engineer to visualize and therefore describe what is actually taking place within the membrane.

In the model demonstrated, it was assumed that the dynamic phase of the membrane was transported by a pressure driven mechanism, similar to what is observed in porous solids. The electrostatic, gravitational and concentration effects were deemed insignificant as the fluid was not considered to be concentrated (thereby negating particle-particle interactions) or of sufficient mass to succumb to gravity's pull. The pore sizes ranged from 2 to 10 nm thereby enabling laminar flow and it can be seen that transport of reagents would be dependent on the availability of nano-sized pores that would connect the anode and cathode. In addition, the highest velocity observed was 9.8467 ms^{-1} , with velocities typically ranging from 2 to 5 ms^{-1} . In this model, the protons are assumed to be carried within the fluid traversing the membrane. If the average velocity within the membrane is taken to be 5 ms^{-1} and the thickness of the membrane $100 \mu\text{m}$ ($\sim 50\times$ the model thickness) the entire membrane can be traversed by a proton in $22 \mu\text{s}$. In figure 4, it was observed that pressures within the membrane increased to $\sim 4 \text{ MPa}$. These high stresses indicate that the membrane may fail if the inlet pressure approaches 1 Atmosphere or that the fluid may not flow.

In the case where the two regions possessed comparable viscosities and densities (see figures 5 and 6), the pressure driven mechanism yields an average velocity of $7.7\times 10^{-5} \text{ ms}^{-1}$ and high negative pressures, approximately $-5\times 10^4 \text{ Pa}$, are observed at the outlet. These values indicate that the second model's assumptions are incorrect, and thus cannot be used to demonstrate proton transport within the aforementioned polymer electrolyte.

6. Conclusions

COMSOL was successfully employed in the visualization of the potential phenomenon occurring in heterocyclic (dry) polymer electrolytes. The mechanism assumed shows that the amorphous state should be sufficiently less dense and viscous than the crystalline to facilitate laminar flow that is dependent on the material's porosity. The next step will be to repeat the process using other scanning electron microscope images of polymer electrolytes. In addition, the geometries will be coupled with different Physics of the Chemical Species Transport module in COMSOL, so as to determine the significance of the effects of concentration gradients and electric fields on charged fluid transport within a given membrane.

7. Acknowledgements

The author would like to thank Mr. Liaquat Ali-Shah (Chief Executive Officer, Caribbean Industrial Research Institute) for providing financial assistance which facilitated participation in this conference.

8. References

1. Spiegel, C. PEM Fuel Cell Modeling and Simulation Using Matlab 2008
2. Springer, T. E. Modeling and Experimental Diagnostics in Polymer Electrolyte Fuel Cells Journal of The Electrochemical Society, ECS, 1993, 140, 3513
3. Bykolu, A. Review of proton exchange membrane fuel cell models International Journal of Hydrogen Energy, 2005, 30, 1181-1212
4. Gurau, V. et al. Two-dimensional model for proton exchange membrane fuel cells AIChE Journal, 1998, 44, 2410-2422
5. Kreuer, K. On the development of proton conducting polymer membranes for hydrogen and methanol fuel cells Journal of Membrane Science, 2001, 185, 29-39
6. Li, Q. et al. Approaches and Recent Development of Polymer Electrolyte Membranes for Fuel Cells Operating above 100 C Chemistry of Materials, American Chemical Society, 2003, 15, 4896-4915
7. Motupally, S. et al. Diffusion of Water in Nafion 115 Membrane Journal of the Electrochemical Society, 2000, 3171-3177

8. Fuel cell fundamentals / Ryan P. O'Hayre ... [et al.]. Hoboken, N.J. : John Wiley & Sons, c2009
9. Bruce, Peter G. Solid State Electrochemistry. Cambridge University Press, 199
10. Stewart, Kerrilee A., Marisa Singh, and Harinder Pal Singh Missan. 2009. Novel PVdF-graft-VIm Based Nano-composite Polymer Electrolyte Membranes for Fuel Cell Applications. In *ECS Transactions*, 25:1459-1468. ECS, September 25.
11. W Münch, K.-D Kreuer, W Silvestri, J Maier, G Seifert, The diffusion mechanism of an excess proton in imidazole molecule chains: first results of an ab initio molecular dynamics study, *Solid State Ionics*, Volume 145, Issues 1-4, 1 December 2001, Pages 437-443, ISSN 0167-2738, 10.1016/S0167-2738(01)00941-9
12. Colomban, P. (1992). Proton Conductors: Solids, Membranes and Gels - Materials and Devices (Volume 2 of Chemistry of Solid State Materials), Cambridge University Press.
13. Schmidt-Rohr, K., & Chen, Q. (2008). Parallel cylindrical water nanochannels in Nafion fuel-cell membranes. *Nature materials*, 7(1), 75-83. doi:10.1038/nmat2074