

Modeling Proton Transport in Hydrophobic Polymeric Electrolytes

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Introduction: This research 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 model. 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.



Figure 1. Hydrophobic polyelectrolyte

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 using the Laminar fluid module.

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. 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 $\frac{1}{4}$ 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).

| 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

| 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

Results:

- 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.
- The highest velocity observed was 9.8467 m/s, with velocities typically ranging from 2 to 5 m/s. 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 m/s and the thickness of the membrane 100 μm (~50 \times the model thickness) the entire membrane can be traversed by a proton in 22 μs .
- In figure 2's pressure profile, it was observed that pressures within the membrane increased to ~4 MPa. These high stresses indicate that the membrane may fail if the inlet pressure approaches 1 Atmosphere or that the fluid may not flow.

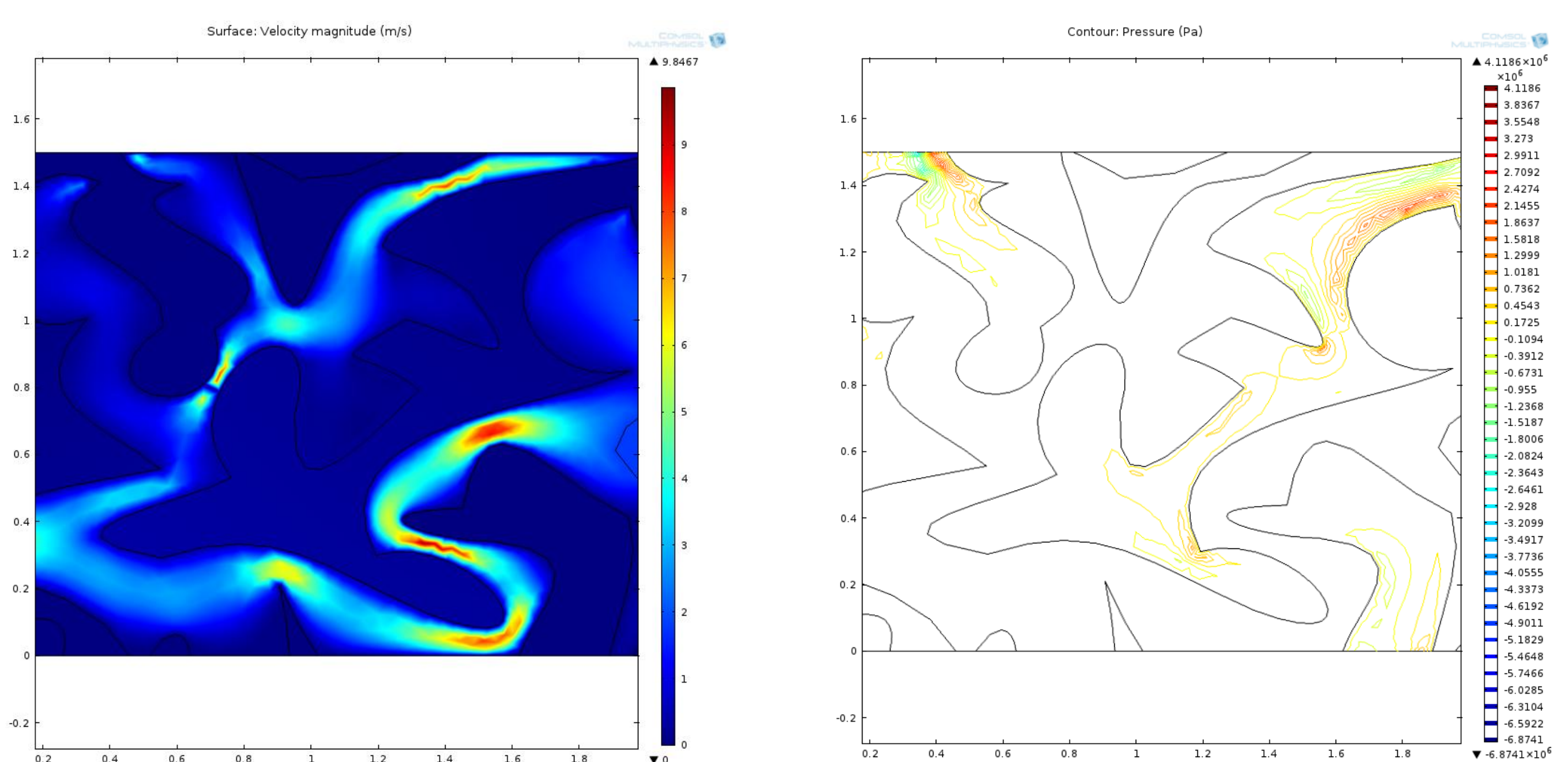


Figure 2. Velocity and pressure profile of steam-like amorphous phase of Poly(vinylidene fluoride)-graft-vinylimidazole

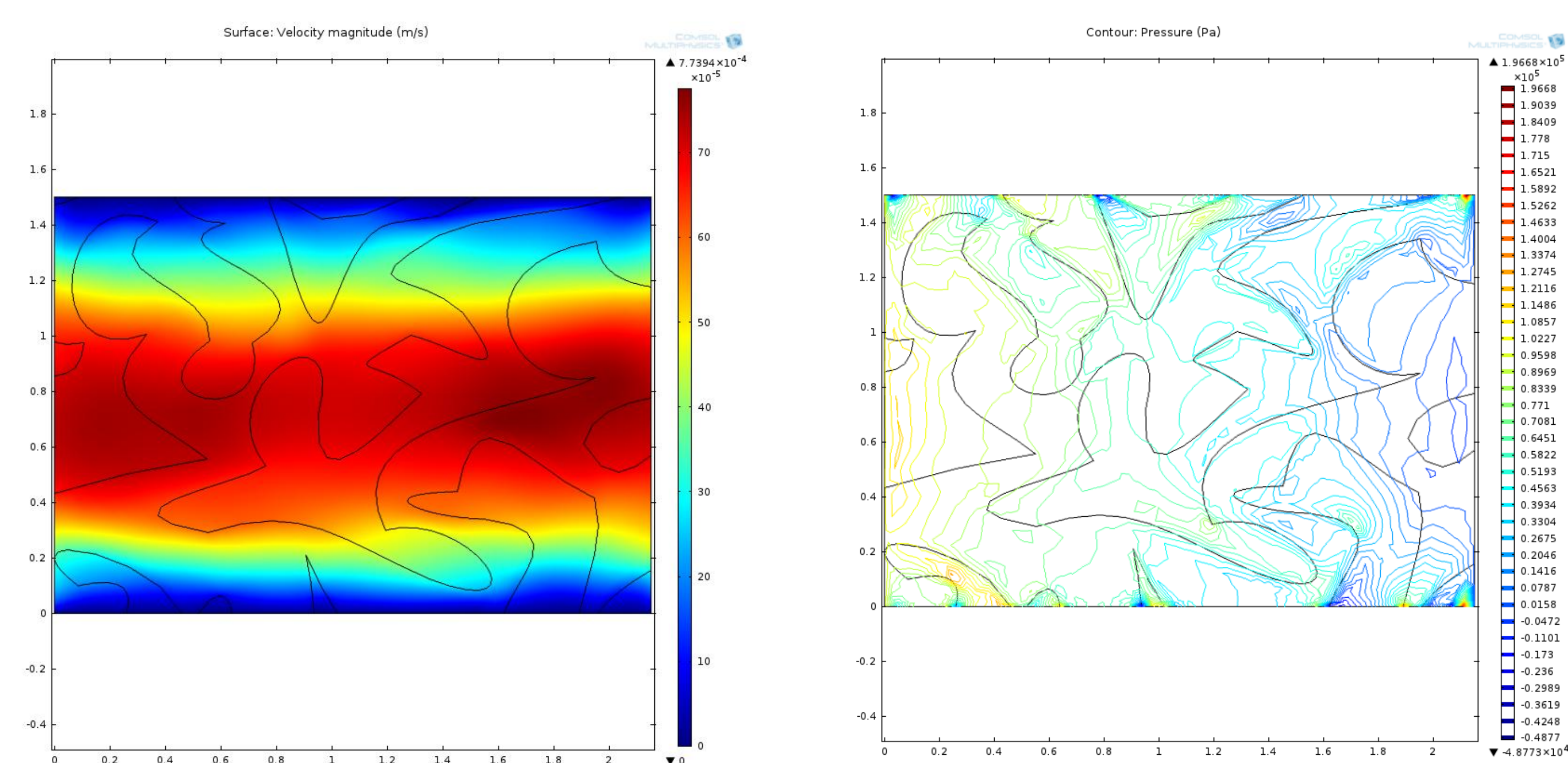


Figure 3. Velocity and pressure profile of polymer-like amorphous phase of Poly(vinylidene fluoride)-graft-vinylimidazole

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