Electrically Triggered Hydrogels: Mathematical Models and Simulations

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ABSTRACT

A chemo-electro-mechanical model has been developed to capture the swelling/deswelling kinetics of electro-responsive gels. The Nernst-Planck equation, the Poisson equation and the mechanical equation are the basic governing equations, which are solved in an iterative manner to compute the concentration of the ions of the various species present in the solution. Electrically triggered hydrogels may be used as components in microfluidic systems.

Keywords: MEMS, Electro-responsive, hydrogels, actuators, microfluidics.

1. INTRODUCTION

Ionic polymer gels have been shown to respond to a number of different stimuli, like pH, electric field, temperature and light. Experiments have been reported on the swelling/deswelling phenomena of hydrogels activated by electric field [1]. Such hydrogels are called electro-responsive gels. Electrically responsive hydrogel (E-gel) based devices may have important applications in the field of artificial organs [2], muscle-like actuators [3] and drug delivery systems [4]. Although the working principle of the E-gels is similar to that of the pH-responsive gels (pH-gels), a major advantage of E-gels over pH-gels is the faster response time of E-gels. E-gels can respond about 1000 times faster than the pH-gels during swelling.

2. THEORY

When an electric field is applied to a salt solution, the ions migrate depending on their charges and the direction of the electric field [5]. Some of the ions may participate in the electro-chemical reactions that take place at the electrodes. Ions such as K^+ and CO_3^{2-} do not undergo electrochemical reactions, and therefore will accumulate near the electrode with opposite charge. The electro-chemical reactions are however important to preserve electro-neutrality. H^+ ions are produced from water at the positive electrode:

$$2H_2O \Rightarrow 4H^+ + 4e^- + O_2 \qquad (1)$$
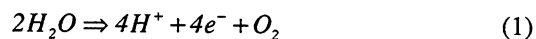
and OH^- ions are produced from water at the negative electrode:

$$4H_2O + 4e^- \Rightarrow 4OH^- + 2H_2 \qquad (2)$$
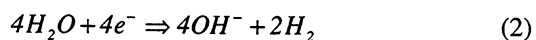
The excess charges produced due to the accumulation of the other ions in the regions near the electrode are neutralized by the H^+ and OH^- ions produced at the electrodes. When a polymer gel is placed in a salt solution and an external electric field is applied, the free ions inside the gel tend to migrate freely. However, the acidic or the basic groups bound to the polymer chains are assumed to be immobile under an electric field [5]. Therefore, their concentration is constant and uniform inside the gel. This in turn retards the migration of the free ions inside the gel to some extent. As a result the ionic concentration gradient inside the gel is much smaller than that in the solution. This redistribution of ionic concentration in both the solution and the gel gives rise to different osmotic pressure at different regions of the gel, which leads to non-uniform swelling of the gel. The osmotic pressure at the anode is found to be higher than that at the cathode. This gives rise to larger swelling of the gel at the anode as compared to the cathode. The electro-responsive gels considered in this work are the HEMA gels.

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3. MATHEMATICAL MODEL

A chemo-electro-mechanical model has been developed to predict the swelling/deswelling kinetics of electro-responsive gels. Owing to the geometry of the polymer gels and the non-uniform swelling under an electric field, a 2D simulation had been done. Figure 1 shows the experimental setup for the electro-responsive gels swelling/deswelling [1]. Simulations have been done for the section AA, which is shown in the top view. Due to symmetry, only the upper half of the section AA has been considered in the simulations. The ring like polymer gel section shown in figure 1 is subjected to a radial osmotic pressure, which varies spatially.
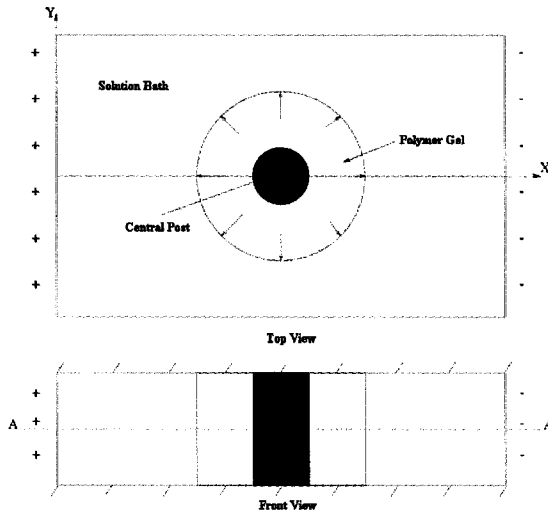

Figure 1: A cylindrical hydrogel with a central supporting post in a channel.

The flux of the kth ionic species in the x-direction Γ_{kx} is described by the Nernst-Planck equation, which includes flux due to diffusion, electrical migration and convection, i.e.,

$$\Gamma_{kx} = \phi\left[-\bar{D}_k\frac{\partial c_k}{\partial x} - \bar{\mu}_k z_k c_k \frac{\partial \psi}{\partial x}\right] + c_k U_x \qquad (3)$$

where ϕ is the gel porosity, $\bar{D}_k$ is the effective diffusivity [6] of the kth ion inside the hydrogel, c_k is the concentration of the kth ionic specie inside the hydrogel, $\bar{\mu}_k$ is the ionic mobility of the kth ion and z_k is the valence of the kth ion. ψ is the electric potential, U_x is the fluid velocity in the x direction and x is the co-ordinate system associated with the deformed hydrogel.

The Einstein relationship [6] relates diffusivity to ionic mobility, i.e.,

$$\bar{D}_k = \frac{\bar{\mu}_k RT}{F} \qquad (4)$$

where R is the universal gas constant, T is the absolute temperature and F is the Faraday's constant. The gel porosity is given by [6]:

$$\phi = \frac{H}{1+H} \qquad (5)$$

where H is the hydration state of the gel and is defined as the ratio of the volume of the fluid to the volume of the solid in the gel.

Similarly, the flux of the kth ionic species in the y-direction, Γ_{ky}, is given by:

$$\Gamma_{ky} = \phi\left[-\bar{D}_k\frac{\partial c_k}{\partial y} - \bar{\mu}_k z_k c_k \frac{\partial \psi}{\partial y}\right] + c_k U_y \qquad (6)$$

The 2D continuity equation for the gel is:

$$\frac{\partial(Hc_k)}{\partial t} = -(1+H)\left[\frac{\partial \Gamma_{kx}}{\partial x} + \frac{\partial \Gamma_{ky}}{\partial y}\right],$$
$$(k = 1, 2,\ldots, N) \qquad (7)$$

where H is the hydration state of the hydrogel, and N is the number of ionic species considered in the solution.

For H$^+$, some of the ions bind to the charged groups inside the gel and are denoted by c_H^b. The continuity equation (7) gets modified for H$^+$:

$$\frac{\partial}{\partial t}\left[Hc_H + Hc_H^b\right] = -(1+H)\left[\frac{\partial \Gamma_{Hx}}{\partial x} + \frac{\partial \Gamma_{Hy}}{\partial y}\right] \qquad (8)$$

The electric field is computed by solving the 2D Poisson equation

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} = -\frac{F}{\varepsilon\varepsilon_0}\left(\sum_{k=1}^{N} z_k c_k + z_f c_f\right) \qquad (9)$$

The mechanical field is given by the following equation:

$$\nabla.\sigma = 0 \qquad (10)$$

where σ is the stress tensor. The various components of the stress tensor are given by the following expressions:

$$\sigma_{xx} = \frac{E}{(1+v)(1-2v)}\left[(1-v)\frac{\partial u_x}{\partial x}+v\frac{\partial u_y}{\partial y}\right]-(P_{osmotic}+\sigma_{electrostatic}) \quad (11)$$

$$\sigma_{yy} = \frac{E}{(1+v)(1-2v)}\left[(1-v)\frac{\partial u_y}{\partial y}+v\frac{\partial u_x}{\partial x}\right]-(P_{osmotic}+\sigma_{electrostatic}) \quad (12)$$

$$\tau_{xy} = \tau_{yx} = G\left[\frac{\partial u_x}{\partial y}+\frac{\partial u_y}{\partial x}\right] \quad (13)$$

$$P_{osmotic} = RT\sum_{k=1}^{N}\left(c_k - c_k^0\right) \quad (14)$$

The effect of electrostatic stress is found to be negligible compared to that of the osmotic stress. However, the present model considers the electrostatic stress in the following way [3]:

$$\sigma_{electrostatic} = k_0\nabla.(k_e\nabla\Psi)\begin{bmatrix}1 & 0\\0 & 1\end{bmatrix} \quad (15)$$

where $\sigma_{electrostatic}$ is the electrostatic stress, k_0 is a material property and k_e is the effective dielectric constant of the polymer.

The present model for electro-responsive gels takes into account the variation of modulus with hydration and applied field. The variation of Young's modulus with changing hydration is given by the following model [7]:

$$E = E_0\frac{(1+H_0)^{1/3}}{(1+H)^{1/3}} \quad (16)$$

Here, E_0 is the initial modulus and H_0 is the initial hydration of the gel.

Besides the effect of hydration, the effect of applied electric field on the modulus is also taken into consideration by the following model [8]:

$$\Delta G = \left(\frac{9}{4}\right)C\varepsilon_1\varepsilon_0\kappa^2 E^2 \quad (17)$$

Where, ΔG is the increase in the shear modulus, C is the volume fraction of the charged particles, E is the electric field, and

$$\kappa = \frac{(\varepsilon_2-\varepsilon_1)}{(\varepsilon_2+2\varepsilon_1)} \quad (18)$$

Here, ε_2 is the relative dielectric constant of the charged particles and ε_1 is the relative dielectric constant of the matrix.

The variation in the modulus with respect to the applied electric field is expected to be significant for an applied electric field of the order of KV/mm. However, in the present cases the applied electric field is of the order of V/mm.

4. RESULTS AND DISCUSSION

Experimental data on swelling/deswelling kinetics of electro-responsive hydrogels were obtained from [1]. The experimental setup is shown in Figure 1. The diameter of the post is 400 μm. The polymer gel jacket thickness before the application of the electric field is 275 μm, and the distance between the electrodes is 2000 μm. The solution was maintained at pH 10, and the ionic concentration was 200 mM with K_2CO_3 as the main salt.

The domain for the simulation of electro-responsive gels is shown in Figure 2. The positive x-y quadrant is the simulation domain. The Finite Cloud Method [9] has been used to solve the governing equations numerically. In the hydrogel area the points are distributed in a circular fashion while the points are distributed in a rectangular fashion in the solution domain.
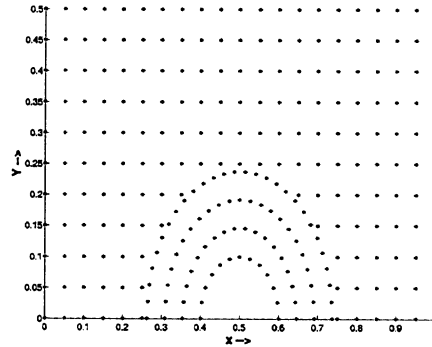

Figure 2: Two dimensional point distribution in the domain of simulation.

The swelling kinetics of the electro-responsive gels is studied for various applied DC voltages across the electrodes. Figure 3 shows the comparison of the simulation results with the experimental results. The agreement is found to be good. As the applied voltage is increased, there is an improvement in the time response of the hydrogel during the swelling phase. During the deswelling phase the voltages are withdrawn

and there is a noticeable dependence on the initial applied voltage (Figure 4). However, due to the lack of any applied voltage during the deswelling phase, the time taken for the deswelling of the hydrogel is observed to be much higher than the time taken for the swelling of the hydrogel.
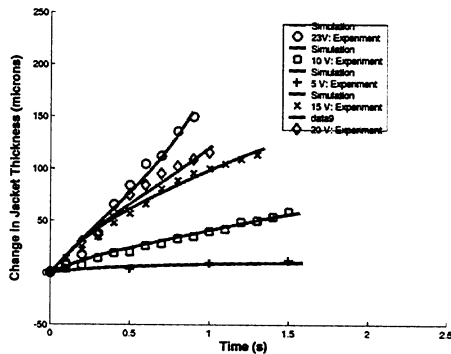

Figure 3: The expansion of the hydrogel in response to different applied voltages. The vertical axis represents the change in the hydrogel jacket thickness relative to the equilibrium thickness.
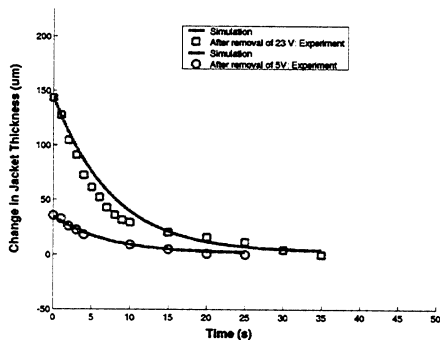

Figure 4: The deswelling of the gels on removal of the applied voltages.

5. CONCLUSION

The results presented in this paper show that electro-responsive hydrogel based devices can be promising for inclusion in a large number of microfluidic systems as valves, pumps or other type of actuators. The time response of the swelling phase is much quicker than that for other stimuli-sensitive hydrogels. There is a significant increase in the amount of swelling of the electro-responsive gels with increasing applied electrical potential difference across the electrodes. Thus, electrical triggering of

hydrogels can prove useful in applications where higher speed is necessary or when precise amount of fluid needs to be measured and dispensed.

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