Mixers and Pumps for Microfluidic Systems, based on Conducting Polymer Oxidation Wave.

Karthik Kannappan[*, 1], Gib Bogle[2], Jadranka Travas-Sejdic[1], and David E. Williams[1]
[1]Department of Chemistry, University of Auckland, [2]Auckland Bioengineering Institute, University of Auckland
*Corresponding author: 23, Symonds Street, Auckland 1010, New Zealand, k.kannappan@auckland.ac.nz

Abstract: Electrochemically-active conducting polymers (ECP) swell or shrink in response to ion and solvent incorporation or ejection as a result of electrochemical reaction of the polymer. As a consequence, they are, in principle, attractive materials to consider for inducing fluid motion of electrolytes in microfluidic systems. When anodic potential is applied to an electrode attached to one end of ECP strip, the oxidation process starts from the electrode and proceeds along the polymer, propagating as a wave. This wave is driven as a consequence of the electrochemical reactions and would be coupled to a propagating front of compositional change. This property of the ECP can be used to design pumps and mixers for microfluidic systems. We in this paper have modeled the oxidation wave propagation and its influence in pumping and mixing of electrolytes in a micro-channel using Comsol 3.5a. The swelling and wave propagation of the conducting polymer was modeled using the moving mesh method (ALE) and we here have solved the coupled convection-diffusion equation and Navier-Stokes equation for finding the velocity and concentration changes in the electrolyte.

Keywords: Conducting polymers, Oxidation wave, Microfluidics.

1. Introduction

When conducting polymers switch between oxidized and reduced state, the conductivity, color and volume undergo significant changes. There is a significant interest to use the volume change property of the ECP to build actuators and mixers for microfluidic devices. Smela et al [1] have summarized the estimates of the magnitude of the volume change that can be achieved in ECP actuators up to 120%, depending on the conditions. There have been attempts to construct actuators and valves utilizing the redox switching and volume change phenomenon of the conducting polymers [2, 3].

These actuators and valves involve complicated fabrication techniques and are somewhat difficult to control. Tezuka and others [4] reported an oxidation wave phenomenon in conducting polymers, where when anodic potential is applied to one end of a polymer strip, the oxidation process starts from that end and propagates as a wave. This oxidation wave would be coupled with a mechanical deformation due to the volume change property of the conducting polymer. We aim to utilize this property of the oxidation wave to design a simple pump for microfluidic devices.

We have constructed a numerical model to determine the conditions under which this surface wave can be made to propagate along the polymer surface. We have linked the effects of geometry of the system, conductivity of polymer/electrolyte and the applied potential to the redox switching and the conductive front wave propagation. We then have used the numerical modeling package COMSOL to design a pump and a mixer utilising this property and have determined its pumping and mixing efficiency.

2. Modelling oxidation wave propagation in conducting polymers

We consider a thin slab of electronically conducting polymer. The polymer slab is in contact with the electrolyte solution. When we apply an anodic potential at one end of the polymer slab it creates a potential gradient initially at one end of the solution. Due to this potential gradient, the polymer will be oxidized, releasing electrons to the external circuit and exchanging ions with the solution in order to balance the charge. The oxidation of the polymer increases its electrical conductivity, so that this part acts as a contacting electrode to the rest of the polymer strip. The process continues until the entire polymer strip is oxidized. Qualitatively, one can observe that the way in which the

polymer transformation propagates along the strip should depend on the conductivity of the polymer in the initial state, whether the polymer conductivity increases or decreases in response to the electrochemical change, and the ion transport in the solution. Under some conditions, the transformation should occur as a wave front propagating along the strip.

This process of the wave propagation has been explained and also been experimentally demonstrated by Tezuka and others [4, 5]. The experimental set up consisted of strip of reduced conducting polymer on a non conductive glass with one end clamped to a metal electrode. When an anodic potential was applied to the metal electrode an oxidation wave proceeded from the metal electrode end to the other end of the film.
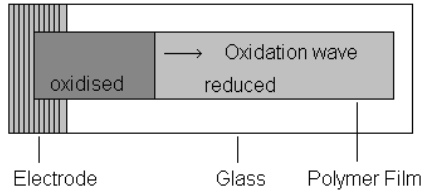

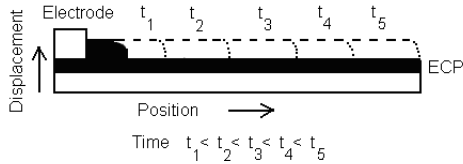**Figure 1**. Oxidation wave (Tezuka et al. experimental setup)

Figure 2. Oxidation wave with polymer swelling

In their experiment the oxidation wave was observed by measuring the film absorbance to a monochromatic light beam. Tezuka et al explained this phenomenon qualitatively. Madden and Warren [6] addressed the results of Tezuka et al and simulated the behavior using an empirical variable resistance transmission line model. Rather than adopt the empirical approach of Madden and Warren, we have developed and solved a complete 2-D model.

We have developed a mathematical model for the two dimensional geometry represented in fig 3. The following assumptions were made to derive the equations. The polymer layer is considered long in comparison to its thickness and is assumed to be uniform in composition in the z direction (right angles to its long axis). The ion exchange reaction at the polymer solution interface is assumed to be at equilibrium, so that the potential difference across the polymer solution interface at any position is given by the Nernst equation applied at that position. The electrolyte solution (represented as A^+B^-) has an initial concentration C_0 For simplicity; all the equations derived here assume that A^+ and B^- are the only ions in the solution. To keep system electrically neutral and balanced, we consider that the negative ion is injected from counter electrode to balance that absorbed into the polymer.

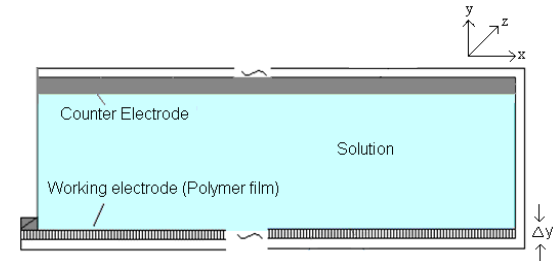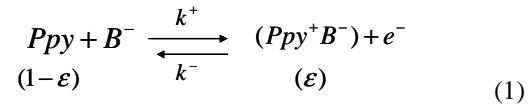The redox reaction of the polymer can be represented by equation (1)

$$Ppy + B^- \xrightarrow[k^-]{k^+} (Ppy^+B^-) + e^-$$
$$(1-\varepsilon) \qquad\qquad (\varepsilon) \tag{1}$$

Figure 3. Geometry of the model

Where ε is the degree of oxidation. When a potential difference is created at the interface, the polymer is oxidized (or reduced), releasing (or consuming) electrons from the external circuit. Balancing this electron flux, there is a flux of negative ions into (or out of) the polymer. The local current density in the solution is related to the rate of oxidation of the polymer which in turn is directly related to the flux of the ions into the polymer. Hence the local current density in the solution is given by

$$i_{Sy} = M F \Delta y \frac{\partial \varepsilon}{\partial t} \tag{2}$$

Where F is the Faraday constant, M is the ion capacity of the polymer film expressed in Moles.m^{-3}, and i_{sy} is the current density in the y-direction (the surface normal) at the interface and Δy is the polymer layer thickness. Equation (2) expresses the assumption of uniformity of composition of the polymer in the y-direction. Note that the width in the z-direction, w, is assumed sufficiently large that the problem can be considered as a 2-D one, with variations only along the x- and y-axes. Similarly there will be a current flow I_P along the length of the polymer, removing the charge consumed by oxidation resulting from the ion flux into the polymer.

$$\frac{\partial I_P}{\partial x} = -i_{Sy} w \tag{3}$$

The potential gradient in the polymer film is determined by this current I_P:

$$\frac{\partial \phi_P}{\partial x} = -\left(\frac{\rho}{w\Delta y}\right) I_P \tag{4}$$

Where ρ is the resistivity of the polymer, which varies with the state of oxidation of the film. (Note that i_{sy}, I_P, ϕ_p and ρ are all functions of x.) Feldman [7] and others [8] suggest that the resistivity switches from a very high (insulating) to a very low (conducting) value when the state of oxidation increases. Warren and Madden [6] propose an empirical sigmoidal function model from which we can determine the conductivity σ_p of the polymer from its fractional oxidation state.

$$\sigma_P = \frac{\sigma_{max} - \sigma_{min}}{1 + e^{(\varepsilon - \varepsilon_T)/W_T}} + \sigma_{min} \tag{5}$$

Where ε_r is the oxidation state at which the transition occurs and W_T is the transition width. The oxidation state and hence the conductivity varies along the length of the polymer.

The Nernst-Planck equation describes the dynamics of ion transport under the influence of an applied electric field and diffusion. Now to solve for the potential distribution in the solution one has to solve Poisson's equation along with this equation. In practice the high degree of non-

linearity of these equations, and the very different distance and time scales of variations in the potential and variations in the concentration make it difficult to solve the resulting set of equations numerically. So we here use an approximate method to handle this situation, developed by Cohen and Cooley [9] for the 1-D case. We have adapted their method to solve our 2-D problem.

The key assumption made by Cohen and Cooley is charge neutrality, i.e. the concentrations of the positive and negative ions remain the same through most of the bulk solution. Thus we derive the equations (6) and (7) and (8)

$$\frac{\partial C}{\partial t} = D_A \nabla^2 C + U_A \nabla \cdot (C \nabla \phi_S) \tag{6}$$

$$i_{Sy} = (J_A - J_B) F \tag{7}$$

$$(U_A - U_B)\frac{RT}{F}\nabla^2 C$$
$$+ (U_A + U_B)\nabla \cdot (C\nabla \phi_S) = 0 \tag{8}$$

The polymer potential ϕ_p and the polymer current I_P together satisfy Ohm's law (4), where the resistivity ρ is a function of ε (ρ is the inverse of σ_p which is given by (5)). The reaction at the polymer solution interface is assumed to be at equilibrium so the potential difference across the interface, ϕ_p -ϕ_s is assumed given by the Nernst equation (9)

$$\phi_p - \phi_s = \Delta\phi^{01} - \frac{RT}{F}\ln\left(\frac{C_B(1-\varepsilon)}{C_0\varepsilon}\right) \tag{9}$$

For a given set of boundary conditions, the coupled equations (2), (3), (4), (5), (6), (7), (8) and (9), completely describe the time evolution of the system. The non-linear time-dependent partial differential equations linking the spatial distributions of potential, ionic concentrations, and polymer oxidation are solved in Matlab using the Scharfetter-Gummel finite difference method. These methods are based on approaches developed in semiconductor analysis [10] and bio-physics [9]. The results show how the polymer oxidation evolves with time over the simulation.

2.1 Results and discussion determining oxidation wave properties:

The ratio of the electrolyte conductivity to the minimum polymer conductivity determines the shape and velocity of the wave propagation (Figure. 4, 5). Solution concentration determines the electrolyte conductivity and minimum conductivity of the polymer depends on its properties. Here length of the polymer is 1cm and the distance between electrodes is 1mm. When the applied voltage was increased the average velocity of the wave increased linearly (Fig.6)
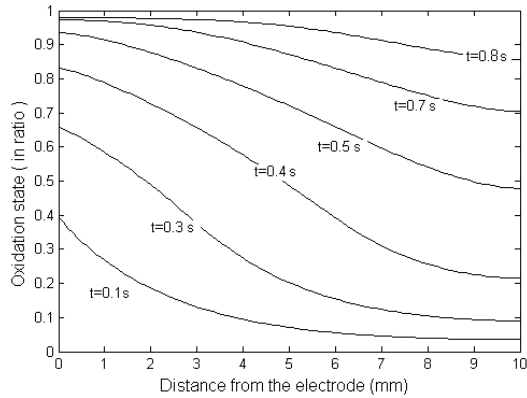
Figure 4. Variation of oxidation wave shape when electrolyte to minimum polymer conductivity is 0.001

The reverse process results in a uniform contraction of the polymer. The reason is that the switch is from a high conductivity state to a low conductivity state, so the current is initially distributed uniformly across the polymer surface [6].

The two dimensional numerical model helps us to understand the oxidation wave process in conducting polymers. It can be used to describe the effects of various parameters such as the concentration of the solution, conducting polymer properties, geometry of the cell and the applied voltage and to determine the conditions at which oxidation wave can be made to propagate along the conducting polymer surface. Thus by varying the properties of electrolyte, polymer, applied voltage and geometry we can control the shape and velocity of the propagating

oxidation wave and that implies we can control the shape and properties of the polymer swelling
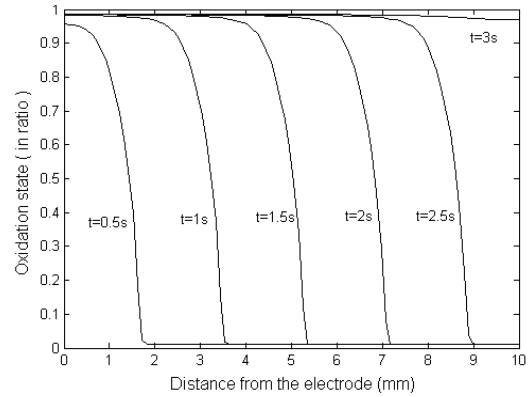

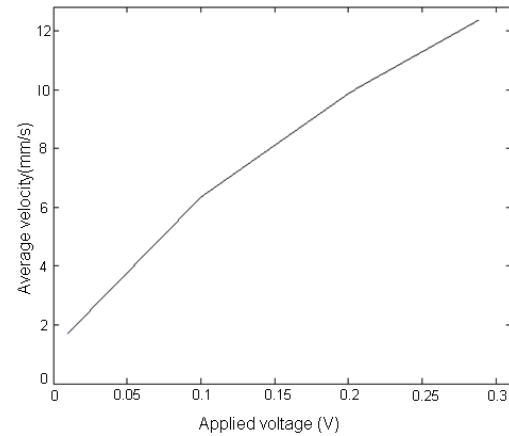**Figure 5.** Variation of oxidation wave shape when lectrolyte to minimum polymer conductivity is 1

Figure 6. Variation of oxidation wave velocity with applied voltage

3. Design of a micro-pump:

In this section we have designed a micro-pump utilising the oxidation wave property discussed in the previous sections. We then find out the pumping rates by varying two different parameters of the pump namely, thickness of polymer swelling and slope of the propagating wave front. Rather than use the exact wave shape derived from the previous analysis, we have simplified the problem by approximating the wave front as a sigmoidal function. We have used the finite element method to solve the Navier-stokes equation to predict the fluid velocity in the microchannel. This method gives us a fair idea of the fluid movement in the channel and ways to optimize the channel to

obtain the desired pumping volume. Here we have designed a 30 micrometer thick channel with conducting polymer strips in the base of the channels. The model was created using Comsol 3.4 multiphysics finite element solver.
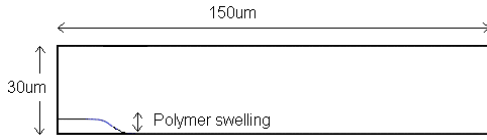

Figure 7. Geometry of the microchannel modelled

We have solved the incompressible Navier-Stokes equation (10) for the 2D domain illustrated in Figure 7.

$$\rho \frac{\partial v}{\partial t} + \rho v \cdot \nabla v = \nabla(-p + \eta(\nabla v))$$

(10)

Where v is the velocity vector, p is the pressure, ρ is the density, and η is the viscosity. We also solved the mass continuity equation (11) along with the Navier-Stokes equation.

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho v) = 0$$

(11)

All the boundaries were considered as no slip boundaries except for the inlet and outlet. The inlet and outlet were set as open boundaries with zero stress.
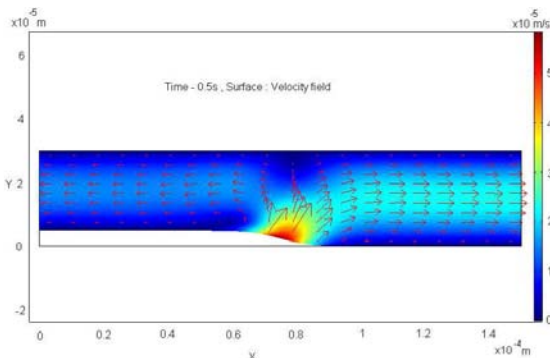

Figure 8. Comsol simulation results showing velocity field of the fluid.

The boundary that defines the polymer swelling was made into a moving mesh boundary with y displacement defined by equation (12)

$$y(x,t) = A - \frac{A}{1 + e^{(x-V*t)/S}}$$

(12)

Where A is the amplitude of the polymer swelling, V is the velocity and S defines the slope of the advancing wave. Here we have set the polymer swelling to move with a defined velocity (V) of 150μm/s. We assume the channel width to be same as the height of the channel, which is 30μm: that is, a chamber volume of 135pL, which is swept by the polymer wave in 1s.
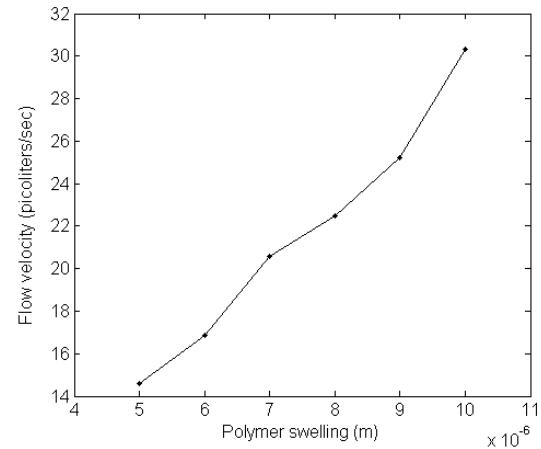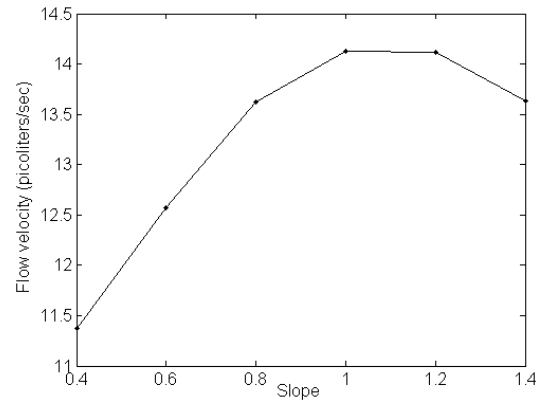

Figure 9. Variation in flow rate with amount of polymer swelling and slope of the surface wave.

From the simulations we were able to predict the maximum flow rate that can be achieved using this design, which was around 30 picoliters per sec, or approximately 22% of the chamber volume in each pass of the wave. The flow rate peaked when the slope of the wave was around 45 degrees and it increased linearly with the polymer swelling (Figure 9.)

4. Design of a micro-mixer:

In this section we have designed a micromixer which utilizes the oxidation wave property of the conducting polymer. We have a designed a configuration where we have two different conducting polymers on either side of the microchannel. Potential can be applied to both of the polymers in such a way that when one polymer is oxidized the other is reduced or vice versa. So when there is an oxidation wave i.e. the mechanical swelling of the polymer at one wall of the channel, the other side is getting reduced, shrinking uniformly[6] maintaining the total volume of the chamber constant. With this configuration there will be negligible amount of fluid that will be transported out of the mixing chamber. We modelled the mixing chamber as a microchannel filled with two different concentrations of liquids, with 0.1moles/litre in the upper half of the microchannel and 0.01 moles/ litre on the lower half of the microchannel.

The mixing of the two different concentrations can be quantified using the diffusive flux across the channel, higher the diffusion more the mixing. We measured the average diffusive flux across the middle of the channel (Observed point) over the time and found that the diffusive flux increased when the wave passes the observed point (at time=0.5s) and thus increasing the mixing. We assume that the mechanical wave pushes material towards the centre of the channel, increasing the concentration gradient and hence increasing the diffusive flux.
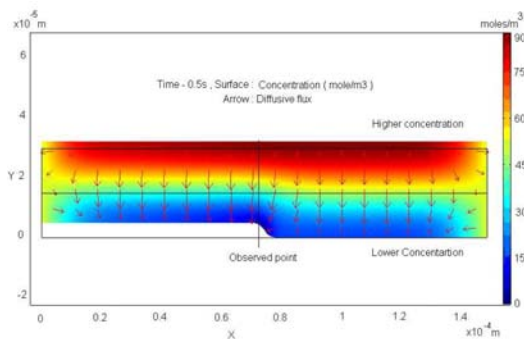

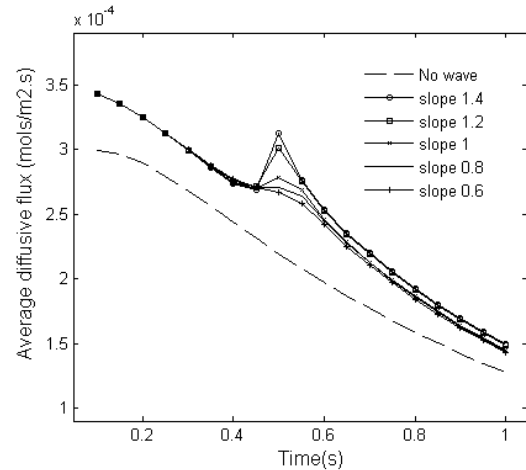**Figure 11.** Mixer geometry with two different concentrations showing the observed point.

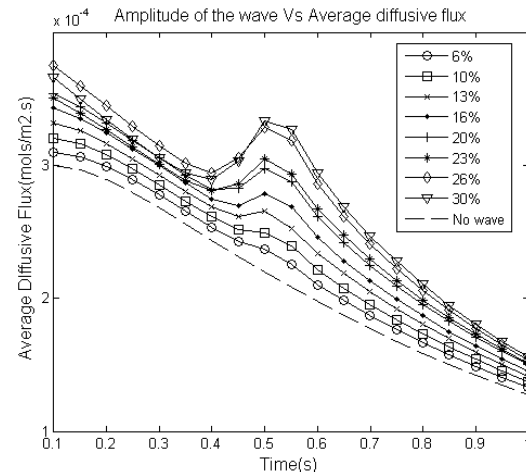**Figure 12.** Variation of the diffusive flux with the slope of mechanical surface wave.

Figure 13. Variation of the diffusive flux with the amount of swelling polymer.

From the simulations we observe that the diffusive flux increases with the slope of the surface wave. The reason for that is when the slope is higher, the rate at which the boundary of the channel moves in y direction i.e. towards the centre of the channel, increases. This increases the convective flux which moves the material towards the centre and thereby increasing the diffusion, thereby improving mixing. The graphs in Figure 12 and Figure 13 also show the diffusive flux when there is no surface wave
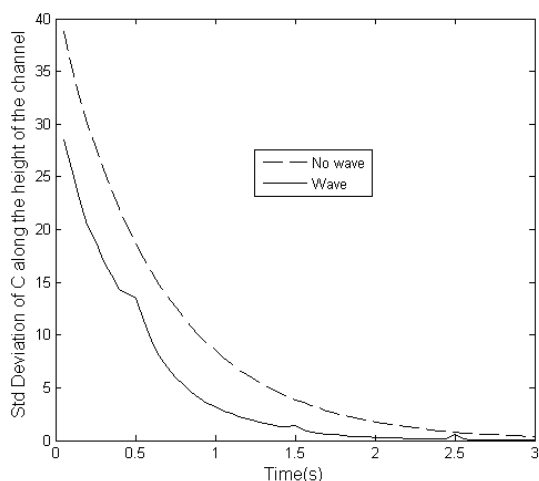
Figure 14. Variation of the concentration difference across the channel over multiple cycles of wave.

The concentration across the channel was also measured over multiple cycles of wave. The standard deviation of the concentration across the channel goes down over time as the two different concentrations across the channel start to mix. We see an increase in the slope as the wave passes through thus increasing the mixing. (Figure 14).

5. Conclusion:

A propagating wave of deformation of an electrochemically-active conducting polymer can be launched along a polymer strip as a consequence of the electrochemical reaction. The shape of the wavefront and its velocity depend upon the relative conductivities of the electrolyte and of the polymer in its oxidised and reduced states. A key element determining the wave propagation is the proportion of the ionic flux in the solution near the interface that is carried by electro-migration rather than diffusion. A micropump and a micromixer can be designed that utilises this phenomenon.

6. References

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