

Supplementary information

S1. Solver sequence:

The non-linear time-dependent partial differential equations linking the spatial distributions of potential, ionic concentrations, and polymer oxidation are solved in Matlab using finite difference methods. The complete code is given in S10. The parameters are solved separately in the sequence explained in figure 1. Solution concentration and oxidation state values are stepped through time and all the other parameters are updated instantaneously. The finite

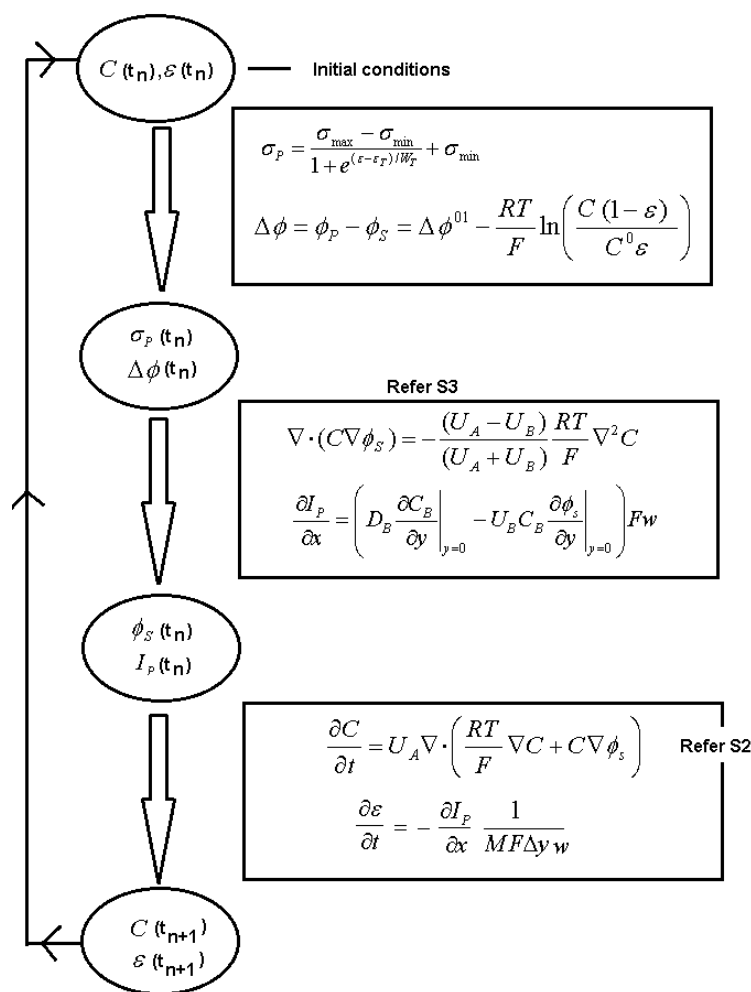


Figure 1. Solver sequence used to solve the partial differential equations

difference schemes used to solve solution potential, polymer current and solution concentration are explained in the following sections. Splitting up the solution of this complex non-linear system into separate steps makes the problem tractable, but in some cases the disconnection between the concentration and potential solvers can lead to ripples that tend to grow. This effect is readily suppressed with a simple smoothing procedure. Holding the end-point values fixed, a sliding-average smoother is applied to each row of the concentration matrix, not touching the rows near the upper and lower boundaries. There undoubtedly are more sophisticated iterative solution procedures that will not require this smoothing step.

S2. Scharfetter-Gummel scheme and Alternating Direction Implicit method:

In order to solve the convection-diffusion problem for concentration over time with the finite difference method (Eq.5 in main article), we use the Scharfetter-Gummel scheme. This exponential fitting discretization method converges faster than the conventional equidistance central difference method and it can handle rapid variations of concentration between two mesh points. This method is derived assuming that the potential gradient is constant between grid points, and has the virtue of guaranteeing mass conservation. We first derive this scheme for a positive ion in one dimension and then extend it to 2-D using the Alternating Direction Implicit method. The drift diffusion equation for the positive ion in one dimension is given by

$$\frac{\partial C}{\partial t} = U \frac{\partial}{\partial x} \cdot \left(\frac{RT}{F} \frac{\partial C}{\partial x} + C \frac{\partial \phi}{\partial x} \right)$$

Here C is the concentration of the ion, and ϕ is the voltage potential.

The original dimensions of the system are normalized using the following parameters.

$$C_0 = 0.1 \text{ (moles L}^{-1}\text{, the bulk concentration)}$$

$$x_0 = 0.001 \text{ (meters, typical width of the system)}$$

$$D_A = D_B = D = 2 \times 10^{-9} \text{ (m}^2\text{s}^{-1}\text{, diffusion constant)}$$

$$t_0 = \frac{x_0^2}{D} \text{ (s, as unit time)}$$

$$\phi_0 = \frac{RT}{F} \text{ (V)}$$

(T is absolute room temperature, R is the gas constant and F is Faraday's constant)

The non-dimensionalised form of the equation is

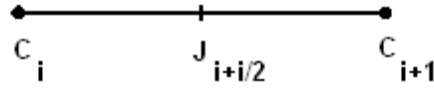
$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \cdot \left(\frac{\partial C}{\partial x} + C \frac{\partial \phi}{\partial x} \right)$$

This can also be written as

$$\frac{\partial C}{\partial t} = - \frac{\partial J}{\partial x} \tag{1}$$

Where $J = - \left(\frac{\partial C}{\partial x} + C \frac{\partial \phi}{\partial x} \right)$ is the flux of the positive ion.

The x axis is discretized with $NX+1$ equally spaced points, $i=1 \dots NX+1$, with spacing Δx . Consider two points i and $i+1$, where the concentrations are C_i and C_{i+1} . The flux between the two grid points is assumed to be constant, $J_{i+1/2}$.



We assume that the potential gradient between the two grid points is constant, and refer to it as K

$$K = \frac{\partial \phi}{\partial x}$$

$$J_{i+1/2} = - \left(\frac{\partial C}{\partial x} + CK \right)$$

Then the variation in concentration between points i and $i+1$ is given by

$$\frac{\partial C}{\partial x} = -KC - J_{i+1/2} \quad (2)$$

Let

$$W_i = C + \frac{J_{i+1/2}}{K}$$

Then we can write Eq.2 as

$$\frac{\partial W_i}{\partial x} = -KW_i$$

Therefore

$$W_i = Ae^{-K\Delta x}$$

Where A is the constant of integration, which we can remove:

$$\frac{W_{i+1}}{W_i} = \frac{Ae^{-K(i+1)\Delta x}}{Ae^{-K(i)\Delta x}} = e^{-K\Delta x}$$

$$\frac{C_{i+1} + \frac{J_{i+1/2}}{K}}{C_i + \frac{J_{i+1/2}}{K}} = e^{-K\Delta x}$$

$$J_{i+1/2} = \frac{-K(C_i - e^{K\Delta x} C_{i+1})}{(1 - e^{K\Delta x})}$$

$$J_{i+1/2} = -\frac{K}{(1 - e^{K\Delta x})} C_i + \frac{Ke^{K\Delta x}}{(1 - e^{K\Delta x})} C_{i+1}$$

$$J_{i+1/2} = \alpha C_i - \beta C_{i+1} \quad (3)$$

Where $\alpha = -\frac{K}{(1 - e^{K\Delta x})}$ and $\beta = -\frac{Ke^{K\Delta x}}{(1 - e^{K\Delta x})}$

Thus we have the flux between the two grid points, given the concentrations at the grid points and the assumed constant potential gradient K . Now the equation 1 can be converted into finite difference formulation and can be solved numerically as below. Consider three points: $i-1$, i , and $i+1$.

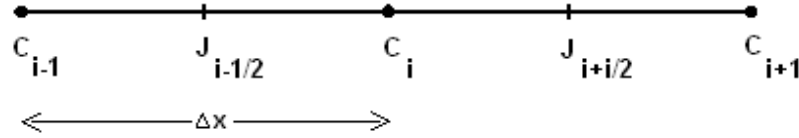


Figure 2. Scharfetter-Gummel 1-D discretization

The equation $\frac{\partial C}{\partial t} = -\frac{\partial J}{\partial x}$ can be written in finite difference form as

$$\frac{\partial C}{\partial t} = -\frac{(J_{i+1/2} - J_{i-1/2})}{\Delta x}$$

Then substituting Eq.3 $J_{i+1/2} = \alpha C_i - \beta C_{i+1}$ and $J_{i-1/2} = \alpha C_{i-1} - \beta C_i$ we get

$$\frac{\partial C}{\partial t} = -\frac{(\alpha C_i - \beta C_{i+1} - \alpha C_{i-1} + \beta C_i)}{\Delta x}$$

$$\frac{\partial C}{\partial t} = -\frac{(\alpha + \beta)C_i - \beta C_{i+1} - \alpha C_{i-1}}{\Delta x}$$

Here we use the implicit finite difference method for time domain discretization. By incrementing from the time step n to $n+1$ we have the following discretization.

$$\frac{C_i^{n+1} - C_i^n}{\Delta t} = \frac{\left[-\frac{(\alpha + \beta)C_i^{n+1} - \beta C_{i+1}^{n+1} - \alpha C_{i-1}^{n+1}}{\Delta x} \right] + \left[-\frac{(\alpha + \beta)C_i^n - \beta C_{i+1}^n - \alpha C_{i-1}^n}{\Delta x} \right]}{2}$$

$$\begin{aligned}
 C_i^{n+1} + \frac{\Delta t}{2} \left[\frac{(\alpha + \beta)C_i^{n+1} - \beta C_{i+1}^{n+1} - \alpha C_{i-1}^{n+1}}{\Delta x} \right] = \\
 C_i^n + \frac{\Delta t}{2} \left[- \frac{(\alpha + \beta)C_i^n - \beta C_{i+1}^n - \alpha C_{i-1}^n}{\Delta x} \right] \\
 \left(1 + \frac{\Delta t}{2\Delta x} (\alpha + \beta) \right) C_i^{n+1} - \frac{\Delta t}{2\Delta x} \beta C_{i+1}^{n+1} - \frac{\Delta t}{2\Delta x} \alpha C_{i-1}^{n+1} \\
 = \left(1 - \frac{\Delta t}{2\Delta x} (\alpha + \beta) \right) C_i^n + \frac{\Delta t}{2\Delta x} \beta C_{i+1}^n + \frac{\Delta t}{2\Delta x} \alpha C_{i-1}^n \quad (4)
 \end{aligned}$$

This equation is the finite difference formulation, where $\alpha = -\frac{K}{(1-e^{K\Delta x})}$, $\beta = -\frac{Ke^{K\Delta x}}{(1-e^{K\Delta x})}$ and

$K = \frac{\partial \phi}{\partial x}$. Note that K , α , and β are computed for each grid interval. The ion flux is specified at each boundary, $J_{x=0}$ and $J_{x=1}$. We need to derive a special form of the equation for these points. At the left boundary $x=0$

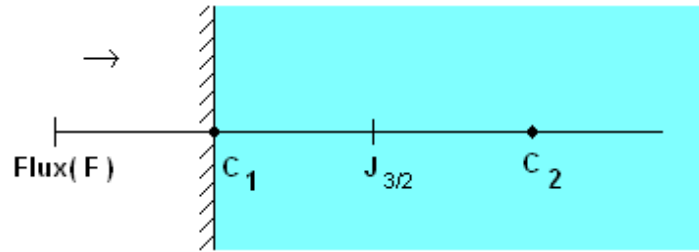


Figure 3. Flux Boundary at $y = 0$

$$\frac{\partial C_1}{\partial t} = -\frac{\partial J}{\partial x}$$

$$\frac{\partial C_1}{\partial t} = -\frac{(F - J_{3/2})}{\Delta x}$$

$$\frac{\partial C_1}{\partial t} = -\frac{(F - \alpha C_1 + \beta C_2)}{\Delta x}$$

Using the implicit finite difference method for time domain discretization

$$\frac{C_1^{n+1} - C_1^n}{\Delta t} = \frac{\left[-\frac{(F - \alpha C_1^{n+1} + \beta C_2^{n+1})}{\Delta x} \right] - \left[-\frac{(F - \alpha C_1^n + \beta C_2^n)}{\Delta x} \right]}{2}$$

$$\frac{C_1^{n+1} - C_1^n}{\Delta t} = \frac{\left[-\frac{(F - \alpha C_1^{n+1} + \beta C_2^{n+1})}{\Delta x} \right] - \left[\frac{(F - \alpha C_1^n - \beta C_2^n)}{\Delta x} \right]}{2}$$

$$\frac{C_1^{n+1} - C_1^n}{\Delta t} = \frac{\Delta t}{2\Delta x} (-F + \alpha C_1^{n+1} - \beta C_2^{n+1} - F + \alpha C_1^n - \beta C_2^n)$$

$$C_1^{n+1} \left(1 - \alpha \frac{\Delta t}{2\Delta x} \right) + \beta \frac{\Delta t}{2\Delta x} C_2^{n+1} = \left(1 + \alpha \frac{\Delta t}{2\Delta x} \right) C_1^n - \beta \frac{\Delta t}{2\Delta x} C_2^n - \frac{\Delta t}{\Delta x} F \quad (5)$$

This gives us the finite difference formulation for the left boundary.

At the right boundary $x=1$

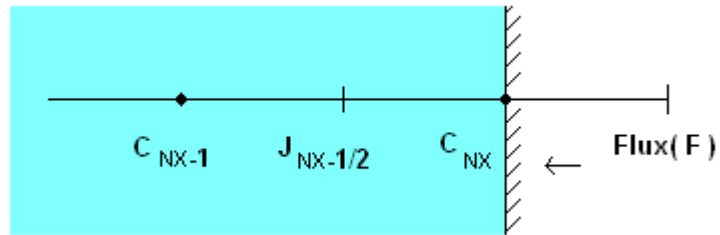


Figure 4. Flux Boundary at $x=1$

$$\frac{\partial C_{NX}}{\partial t} = -\frac{\partial J}{\partial x}$$

$$\frac{\partial C_{NX}}{\partial t} = -\frac{(J_{NX-1/2} - F)}{\Delta x}$$

$$\frac{\partial C_{NX}}{\partial t} = -\frac{(\alpha C_{NX-1} - \beta C_{NX} - F)}{\Delta x}$$

Using the implicit finite difference method for time domain discretization

$$\frac{C_{NX}^{n+1} - C_{NX}^n}{\Delta t} = \frac{-\left[\frac{(\alpha C_{NX-1}^{n+1} - \beta C_{NX}^{n+1} - F)}{\Delta x}\right] - \left[\frac{(\alpha C_{NX-1}^n - \beta C_{NX}^n - F)}{\Delta x}\right]}{2}$$

$$\frac{C_{NX}^{n+1} - C_{NX}^n}{\Delta t} = \frac{\frac{\Delta t}{2\Delta x}(F - \alpha C_{NX-1}^{n+1} + \beta C_{NX}^{n+1} + F - \alpha C_{NX-1}^n + \beta C_{NX}^n)}{1}$$

$$C_{NX}^{n+1} \left(1 - \beta \frac{\Delta t}{2\Delta x}\right) + \alpha \frac{\Delta t}{2\Delta x} C_{NX-1}^{n+1} = \left(1 + \beta \frac{\Delta t}{2\Delta x}\right) C_{NX}^n - \alpha \frac{\Delta t}{2\Delta x} C_{NX-1}^n + \frac{\Delta t}{\Delta x} F \quad (6)$$

At each time step, the set of linear equations given by 4, 5 and 6 can be solved for the concentrations at the $NX+1$ grid points, given the potential Φ as a function of x and the concentrations at the previous time step. The way we solve for P and C together is discussed below in the description of the method used for the 2-D case.

Alternating Direction Implicit method:

Now we can extend this 1-D finite difference method to two dimensions in x and y directions using alternate direction implicit method. Alternating Direction Implicit (ADI) method uses two half step time intervals in order to progress one time step. The time interval Δt is divided into two. During the first half step, from time t to $t + \frac{\Delta t}{2}$ only x direction values are integrated while the y direction values are held fixed. During the second half of the time step i.e. from $t + \frac{\Delta t}{2}$ to $t + \Delta t$ the y direction values are updated using the previous results as base values, while the x direction values are held fixed. Figure 5 is the 5 point ($C_{i,j}$, $C_{i-1,j}$, $C_{i+1,j}$, $C_{i,j-1}$, $C_{i,j+1}$) stencil representation of the system in a two dimensional domain. The fluxes in the system can be represented using the Scharfetter-Gummel method explained above. Using the equation 3 we can derive the fluxes at the points $J_{i-1/2,j}$, $J_{i+1/2,j}$, $J_{i,j+1/2}$, $J_{i,j-1/2}$.

In the x direction the flux depends on the potential gradient along the x direction given by $K_x = \frac{\partial \phi}{\partial x}$ and in y direction it depends on the potential gradient along the y direction given

by $K_y = \frac{\partial \phi}{\partial y}$. Thus the α and β in the equation 3 for x direction are given by $\alpha_x = -\frac{K_x}{(1 - e^{K_x \Delta x})}$

and $\beta_x = -\frac{K_x e^{K_x \Delta x}}{(1 - e^{K_x \Delta x})}$ and for y direction are given by $\alpha_y = -\frac{K_y}{(1 - e^{K_y \Delta y})}$ $\beta_y = -\frac{K_y e^{K_y \Delta y}}{(1 - e^{K_y \Delta y})}$

Thus the fluxes are given by

$$J_{i-1/2,j} = \alpha_x C_{i-1,j} - \beta_x C_{i,j}$$

$$J_{i+1/2,j} = \alpha_x C_{i,j} - \beta_x C_{i+1,j}$$

$$J_{i,j-1/2} = \alpha_y C_{i,j-1} - \beta_y C_{i,j}$$

$$J_{i,j+1/2} = \alpha_y C_{i,j} - \beta_y C_{i,j+1}$$

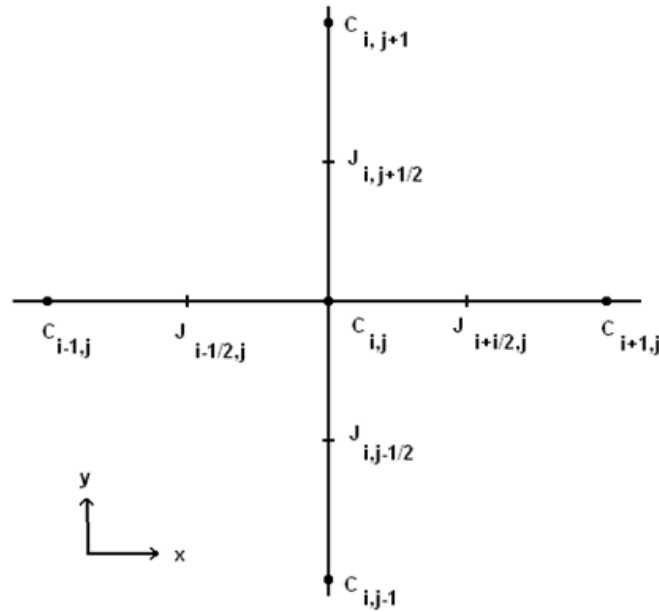


Figure 5. 2-D Stencil for Alternating Direction Implicit method

We know that $\frac{\partial C_{i,j}}{\partial t} = -\nabla \cdot J_A$. This equation is solved implicitly from time n to time n+1.

First the time step is divided into two as n to n+1/2 and n+1/2 to n+1. During the first half of the time step,

$$\frac{C_{i,j}^{n+1/2} - C_{i,j}^n}{\Delta t} = \frac{\left(\frac{J_{i-1/2,j}^{n+1/2} - J_{i+1/2,j}^{n+1/2}}{\Delta x} \right) + \left(\frac{J_{i,j-1/2}^n - J_{i,j+1/2}^n}{\Delta y} \right)}{2} \quad (7)$$

Only the x direction values are integrated over the time while the y direction values are held as same in the previous time step. Over the next half of the time step we use the results from the previous calculation and integrate the system over time only in the y direction while holding the x direction values same. Thus we get the integrated final values in both the directions for the time n+1.

$$\frac{C_{i,j}^{n+1} - C_{i,j}^{n+1/2}}{\Delta t} = \frac{\left(\frac{J_{i,j-1/2}^{n+1} - J_{i,j+1/2}^{n+1}}{\Delta y} \right) + \left(\frac{J_{i-1/2,j}^{n+1/2} - J_{i+1/2,j}^{n+1/2}}{\Delta x} \right)}{2} \quad (8)$$

The boundaries are treated same as the 1D method. The stencil for the lower boundary is given in the figure 6. Here we have a specified flux F instead of $J_{i,j-1}$. The derivation for the lower boundary with the specified flux F is given below in the equations 9 and 10. Similarly we can derive finite difference equations for all the other three boundaries.

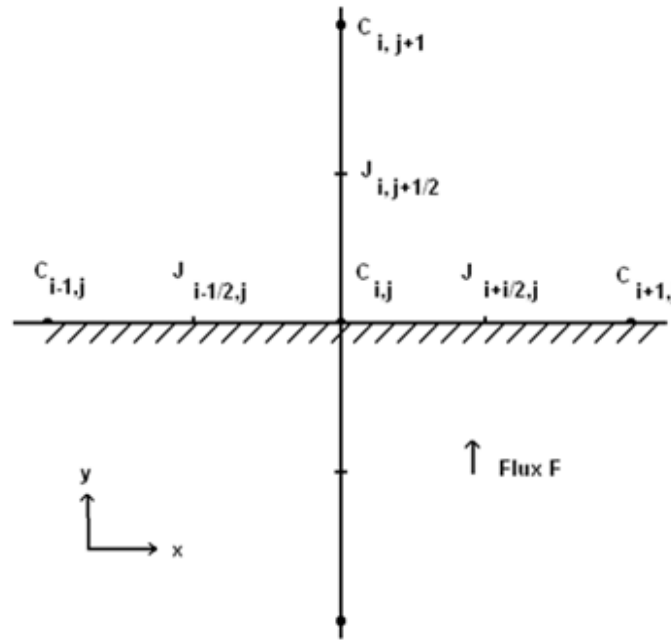


Figure 6. Lower boundary

$$\frac{C_{i,j}^{n+1/2} - C_{i,j}^n}{\Delta t} = \frac{\left(\frac{J_{i-1/2,j}^{n+1/2} - J_{i+1/2,j}^{n+1/2}}{\Delta x} \right) + \left(\frac{F - J_{i,j+1/2}^n}{\Delta y} \right)}{2} \quad (9)$$

$$\frac{C_{i,j}^{n+1} - C_{i,j}^{n+1/2}}{\Delta t} = \frac{\left(\frac{F - J_{i,j+1/2}^{n+1}}{\Delta y} \right) + \left(\frac{J_{i-1/2,j}^{n+1/2} - J_{i+1/2,j}^{n+1/2}}{\Delta x} \right)}{2} \quad (10)$$

The two systems of linear equations that result from the finite difference formulation, one for each half time step, are solved in the usual way. In our current application we solve for the concentration of the positive ion (A), for which the boundary conditions are zero flux on all the boundaries. As discussed in the main text, the concentration of the negative ion B equals the concentration of A everywhere.

S2. Calculating solution potential and polymer current from concentration and ion flux:

Potential in the solution and the polymer current can be calculated from the solution concentration and ion flux at the interface using the following equations (Equations 2, 3, 11, 18 in main article).

$$\nabla \cdot (C \nabla \phi_s) = - \frac{(U_A - U_B)}{(U_A + U_B)} \frac{RT}{F} \nabla^2 C \quad (11)$$

$$\frac{\partial I_P}{\partial x} = -i_{s,y,0} w \quad (12)$$

$$i_{s,y,0} = MF \Delta y \frac{\partial \varepsilon}{\partial t} \quad (13)$$

$$J_{B,0} = M \Delta y \frac{\partial \varepsilon}{\partial t} = - \left(D_B \frac{\partial C_B}{\partial y} \Big|_{y=0} - U_B C_B \frac{\partial \phi_s}{\partial y} \Big|_{y=0} \right) \quad (14)$$

From equations 12, 13 and 14 we arrive at the equation 15, defining polymer current in terms of the ion flux at the interface.

$$\frac{\partial I_P}{\partial x} = \left(D_B \frac{\partial C_B}{\partial y} \Big|_{y=0} - U_B C_B \frac{\partial \phi_s}{\partial y} \Big|_{y=0} \right) F w \quad (15)$$

We have solved equation 11 and 15 together to find I_p and ϕ_s . We use the finite difference method with the matrix formulation described as in figure 7.

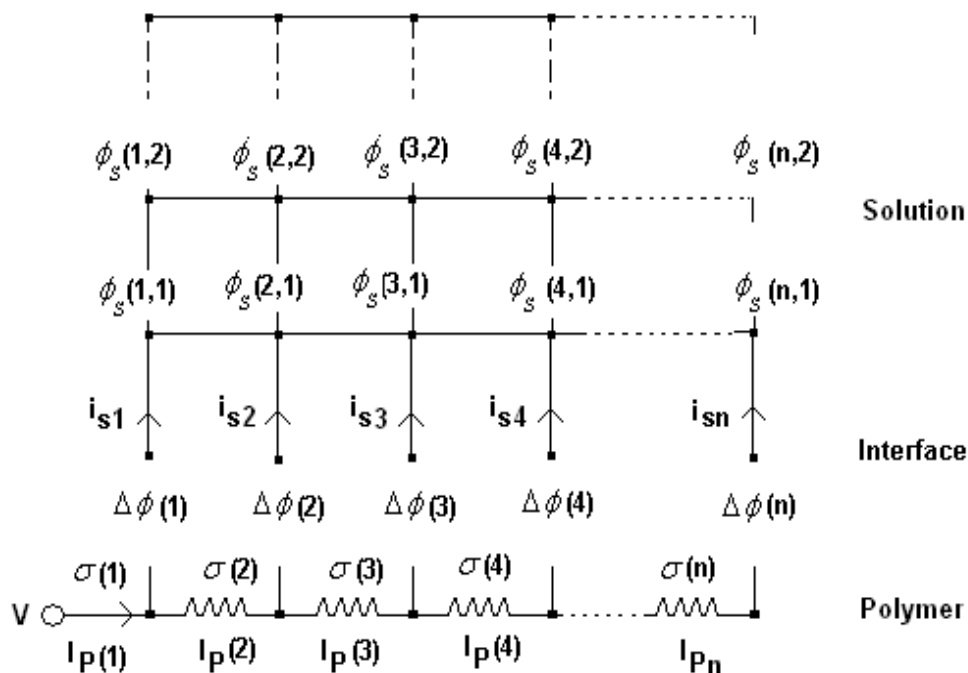


Figure 7. Matrix formulation for solving polymer current (I_p) and solution potential (ϕ_s)

$$\Delta\phi = \phi_P - \phi_S = \Delta\phi^{01} - \frac{RT}{F} \ln\left(\frac{C_B(1-\varepsilon)}{C^0\varepsilon}\right) \quad (16)$$

We solve for the polymer currents $I_p(k)$ at the same time as solving for the solution potential, by including in our linear system equations that combine equation 16 with Ohm's law to relate the polymer currents to the solution potential values at the boundary. In place of the usual stencil, for $\phi_s(k,1)$ equation 15 is used to provide a linear equation linking the I_p values to the solution potential (a three-point formula is used to estimate the gradient of ϕ_s at the boundary). Updating of oxidation ε at each time step is performed using a simple explicit discretization of equation 13.

S4. Video file illustrating time evolution of concentration, potential field, degree of oxidation, current density across the interface, polymer potential and polymer current.

S5. Further results on the modeling of oxidation wave propagation in conducting polymers:

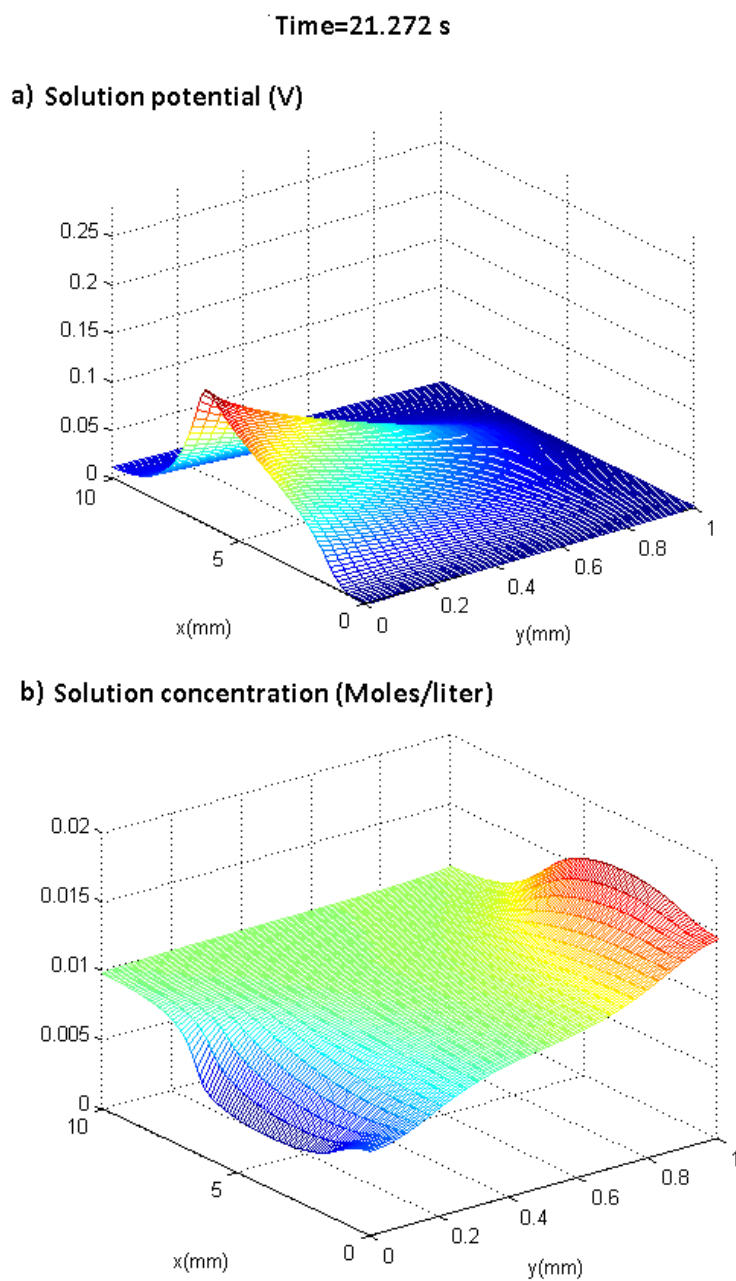


Figure 8. Variation of concentration and potential fields during the simulation

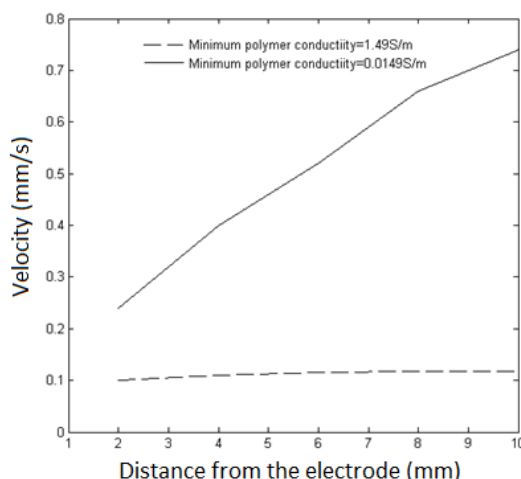


Figure 9. Variation of the velocity along the length of the polymer with different initial conductivities

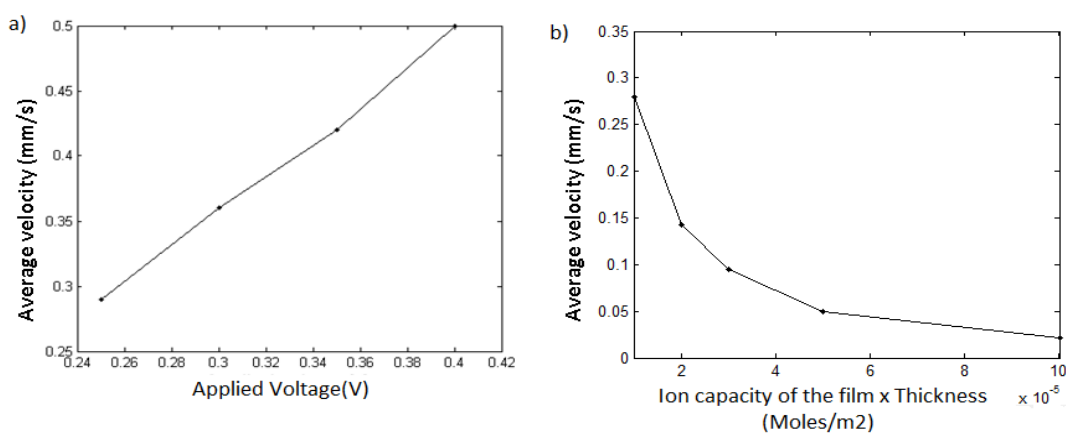


Figure 10. Variation of wave velocity with (a) applied potential and (b) the product of ion capacity of the film times its thickness. Minimum polymer conductivity is 0.149S/m (Other conditions as in Fig 2 in main article)

The oxidation process of the conducting polymer film was associated with strong gradients in the potential and the concentration of the solution which is illustrated in figure 8.

Change in the minimum polymer conductivity changed the shape of the oxidation wave profile and because of that the velocity of the progressing wave also changed. When the initial polymer conductivity is high, the wave accelerates as it progresses along the strip. With decreasing initial polymer conductivity, the wave velocity is significantly lower, the acceleration becomes less marked and the wave velocity becomes relatively constant as shown in figure 9. The velocity of the oxidation wave was linearly influenced by the applied voltage. When we increased the applied voltage the oxidation process was faster and the wave velocity increased, but the velocity was inversely proportional to the ion capacity and thickness of the film. These effects are illustrated in figure 10.

S6. Design of a micro-pump:

In this section, we present the micropump design with conducting polymer on both walls of the microchannel, with each polymer assumed to swell equally. We have used a sigmoidal function to simulate the polymer swelling due to the oxidation wave. Figure 11(a) shows the simulated velocity field during the oxidation wave. The results showed that the pumping rate was linearly proportional to the slope of the wave and the amount of polymer swelling as illustrated in figure 11(b,c).

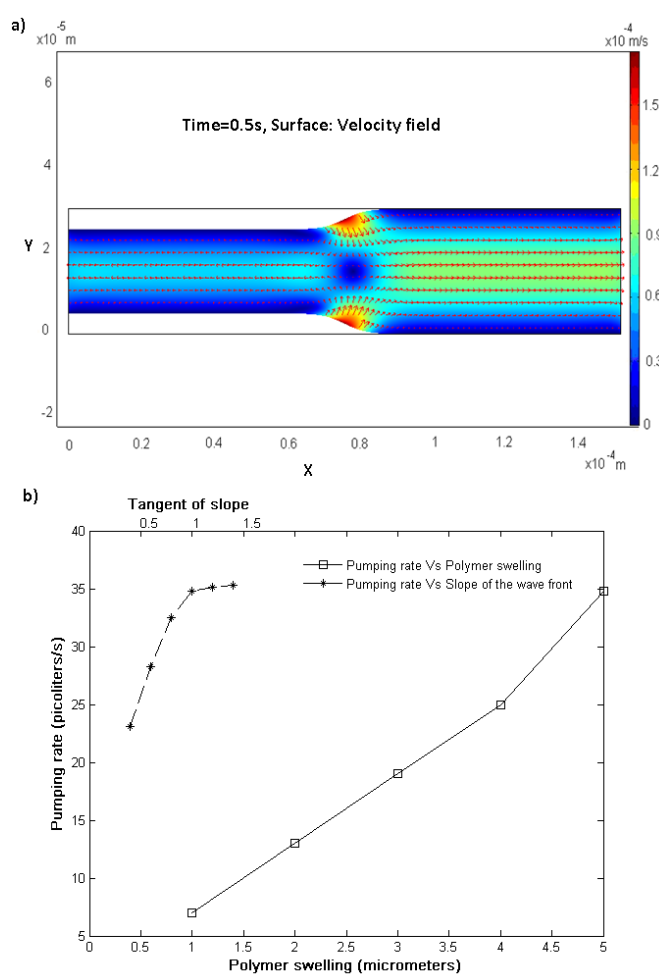


Figure.11 Simulation of micropump behavior with ECP swelling on both faces of the channel. The wave propagates the length of the channel in 1s. (a) velocity field; (b) dependence of pumping rate on expansion with front-slope 45° and on front-slope with expansion $5\mu\text{m}$.

S7. Design of a micromixer:

Figure 12 illustrates that higher the slope of the advancing oxidation wave, higher the

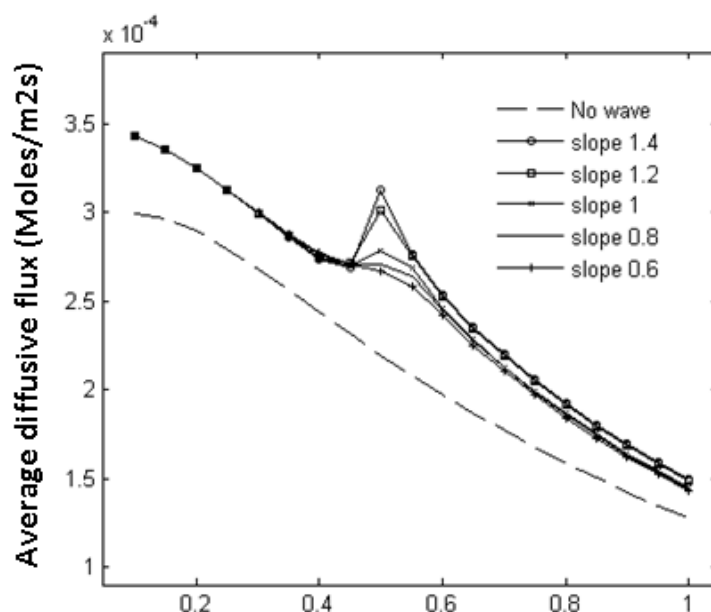


Figure 12. Variation of the diffusive flux with the slope of mechanical surface wave.

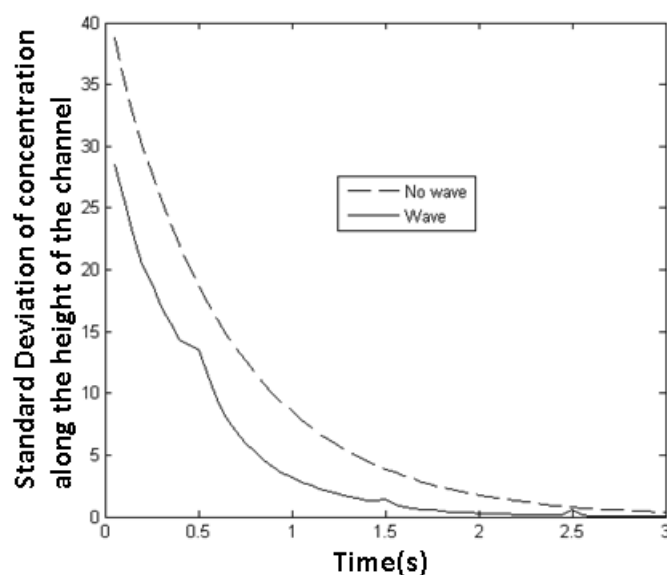


Figure 13. Variation of the concentration difference across the channel over multiple cycles of wave.

diffusive flux and hence higher the mixing. Figure 13 shows the standard deviation of the concentration over multiple cycles of oxidation wave and that complete mixing could be achieved with just 3 cycles and is faster than the normal diffusive mixing.

S8. Video file illustrating the velocity field and velocity vectors during the simulation of a micropump.

S9. Video file illustrating the evolution of concentration field and the direction of velocity vector for the micromixer design.

S10. Matlab code for solution of the diffusion- migration problem in 2-D, using the Scharfetter-Gummel and Cohen-Cooley schemes