On Electroneutrality Condition Inside Solid Conducting Porous Film

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Conducting and ionic polymers are finding many new applications such as bioelectronic devices, drug delivery systems, micro and nano electrodes. An understanding of the various transport processes in thin films of conducting polymers has thus become essential.[1,2] These polymers have substantial porosity and delocalized charge centers, which cause counter-ionic diffusion and electro-migration inside polymeric electrode bodies.[2–6] While electroneutrality is attained very fast in liquid phase, it may take much longer time inside conducting films (even thin films), as the ionic diffusivity is very low in solids. Still electroneutrality is almost always assumed for such systems though it virtually decouples ion concentrations from potential.[7–9] Oldham and Bond[10] has checked electroneutrality assumption for steady-state voltammetry and discussed the reason for the discrepancy between the processes with and without electroneutrality assumption for very small electrodes. Probable deviation from electroneutrality for a cation selective membrane has been studied by Rubinstein.[11] Deviations from local electroneutrality in the region adjacent to the membrane lead to electrodiffusional instability of the steady solutions of the Poisson-Nernst-Planck (PNP) system above a certain critical voltage. Hsu and Li[12] have treated steady-state diffusion in systems similar to the systems studied here using the full PNP framework without assuming electroneutrality. They have pointed out that assumption of electroneutrality causes significantly different results. Another study[13] has shown possible breakdown of electroneutrality condition for electrodes with submicron size regardless of electrolyte concentration. Multiscale diffusion-reaction modeling study has been done by Rotenberg et al.,[14] which shows atomistic plus mesoscopic description for mobility of ions in clay (electrokinetic transport).

In this study, an ‘‘intraelectrode’’ phenomenon, where the electrode (a conducting polymeric film) allows ionic diffusion and migration from adjacent electrical double layer into itself, is investigated. Because of low ionic diffusivities in such polymeric films, ions and counter-ions cannot instantaneously come close and get neutralized. The range of ionic diffusivity inside such conducting polymer matrix has been reported as 10^{-11} to 10^{-15} m^2/s.[6,15] The dynamics of the build up of charge and concentration profiles inside such polymeric electrode is the objective of this study. It has been shown that electroneutrality is not maintained or reached and a charge boundary layer forms inside the CP film adjacent to the double layer. None of the previous studies investigated this boundary layer or the effects of low diffusivity and the finite rates of neutralization together. All these have important effects on applications like controlled drug delivery.

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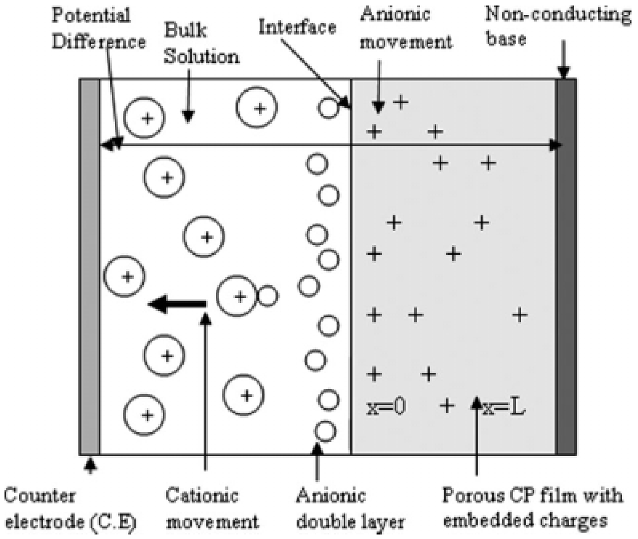

Figure 1. Depiction of the electrochemical thin-film-based molecular release system.

Figure 1 depicts the electrochemical system where conducting polymer thin-film itself acts as the working electrode. The distribution of fixed cationic charges inside the film is assumed to be linear with the highest concentration at the liquid double layer-membrane interface ($x = 0$). A constant interfacial voltage at polymer-double layer interface is also maintained. On the other side of the film, i.e., the non-conducting base-polymer interface ($x = L$), a potential close to zero is maintained. Now, anions should move into the membrane toward the cationic sites inside the film and will get distributed inside membrane by both concentration-driven and electric field-driven fluxes.

The mathematical framework for analyzing the process comprises of the Nernst-Planck (NP) equation with ionic reaction term and the Poisson (P) equation that describes a ''steady'' electric field, completing the PNP framework. The conventional form of Poisson equation is:

$$\frac{d^2E}{dx^2} = -\frac{\rho}{\varepsilon} \tag{1}$$

E = potential; ρ = charge density; and ε = permittivity of the medium.

Disappearance of the cationic sites through reaction with incoming anions can be expressed as follows:

$$\mathrm{A}+ \quad + \quad \mathrm{B}- => \mathrm{AB}; \ \frac{dC_{\mathrm{A}+}}{dt} = -k_{1\mathrm{f}}.C_{\mathrm{A}+}.C_{\mathrm{B}-} \tag{2}$$

$k_{1\mathrm{f}}$ is the kinetic constant, $C_{\mathrm{A}+}$ and $C_{\mathrm{B}-}$ are the cationic and anionic concentrations, respectively. Electromigration, diffusion, and reaction-based balance of anions can be expressed through the Nernst-Planck equation:

$$\frac{\partial C_{\mathrm{B}-}}{\partial t} = -k_{1\mathrm{f}}.C_{\mathrm{A}+}.C_{\mathrm{B}-} + D_{\mathrm{B}-}.\frac{\partial^2 C_{\mathrm{B}-}}{\partial x^2} + \frac{D_{\mathrm{B}-}.Z_{\mathrm{B}-}.F}{R.T} \times \left[\frac{\partial C_{\mathrm{B}-}}{\partial x}.\frac{\partial E}{\partial x} + C_{\mathrm{B}-}.\frac{\partial^2 E}{\partial x^2}\right] \tag{3}$$

$Z_{\mathrm{B}-}$ = valence of anions; $D_{\mathrm{B}-}$ = diffusivity of anions in the polymeric matrix; T = temperature.

''Method of Lines'' approach has been used to solve the NP equation. Runge-Kutta (RK-4) has been used to solve the set of coupled nonlinear ODEs. Thomas algorithm was used to solve discretized Poisson equation to generate the potential field for all the grid points.

At very large time, when all cations have been neutralized, an ''equilibrium'' or ''steady state'' is established and the equations reduce to:

$$D_{\mathrm{B}-}\frac{d^2C_{\mathrm{B}-}}{dx^2} + \frac{Z_{\mathrm{B}-}F}{RT}D_{\mathrm{B}-}\frac{d}{dx}(C_{\mathrm{B}-}\frac{dE}{dx}) = 0 \tag{4}$$

$$\frac{d^2E}{dx^2} = \frac{Z_{\mathrm{B}-}F}{\varepsilon}C_{\mathrm{B}-} \tag{5}$$

F = Faraday constant.

Analytical solution for this set of equations is possible for the boundary conditions: For $x = 0$, $E = E^0$, and $C_{\mathrm{B}-} = C_{\mathrm{B}}{}^0$. For $x = L$, $E = 0$, and no flux condition for $C_{\mathrm{B}-}$.

Now using dimensionless formulation: $x^* = x/L$, $C_{\mathrm{B}}{}^* = C_{\mathrm{B}-}/C_{\mathrm{B}}{}^0$, and $E^* = (Z_{\mathrm{B}-}FE)/\mathrm{RT}$.

By simple algebraic steps, one can write,

$$\frac{d^2 \ln C_{\mathrm{B}}^*}{dx^{*2}} = \frac{d^2E^*}{dx^{*2}} = \frac{C_{\mathrm{B}}^*}{z^*} \tag{6}$$

where $z^* = \frac{\varepsilon RT}{Z_{\mathrm{B}-}^2 C_{\mathrm{B}}^0 F^2 L^2}$ (important intermediate step: $\frac{dC_{\mathrm{B}}^*}{dx^*} - C_{\mathrm{B}}^* \cdot \frac{dE^*}{dx^*} = 0$).

Now, we have $C_{\mathrm{B}}{}^* = 1$ at $x^* = 0$. This equation can be reduced to the following form by algebraic manipulation:

$$\frac{dC_{\mathrm{B}}^*}{C_{\mathrm{B}}^*.(C_{\mathrm{B}}^* + Kz^*/2)^{\frac{1}{2}}} = -(\frac{2}{z^*})^{\frac{1}{2}}.dx^* \tag{7}$$

where K is a constant for integration (important intermediate step: $\frac{d \ln C_{\mathrm{B}}^*}{dx^*} = \left[\frac{2}{z^*}.C_{\mathrm{B}}^* + K\right]^{1/2}$).

This can be integrated further to yield the following solution (for $K > 0$):

$$C_{\mathrm{B}}^* = \frac{K.z^*}{2}.\left[\left(\frac{e^{K^{1/2}.x^*} + M}{e^{K^{1/2}.x^*} - M}\right)^2 - 1\right] \tag{8}$$

and thus

$$E^* = E_0^* + (K^{1/2}.x^*) + \ln\left(\frac{1-M}{e^{K^{1/2}.x^*} - M}\right)^2 \tag{9}$$

where $M = \frac{\left(1+\frac{K.z^*}{2}\right)^{1/2} - \left(\frac{K.z^*}{2}\right)^{1/2}}{\left(1+\frac{K.z^*}{2}\right)^{1/2} + \left(\frac{K.z^*}{2}\right)^{1/2}}$ and $E_0^* = \ln\left(\frac{e^{K^{1/2}} - M}{1-M}\right)^2 - K^{1/2}$.

For $K < 0$:

$$C_{\mathrm{B}}^* = \frac{K.z^*}{2}.\sec^2\left(\alpha - \frac{K^{1/2}.x^*}{2}\right) \tag{10}$$

and

$$E^* = E_0^* + \ln\left(\frac{\cos^2 \alpha}{\cos^2\left(\alpha - \frac{K^{1/2}.x^*}{2}\right)}\right) \tag{11}$$

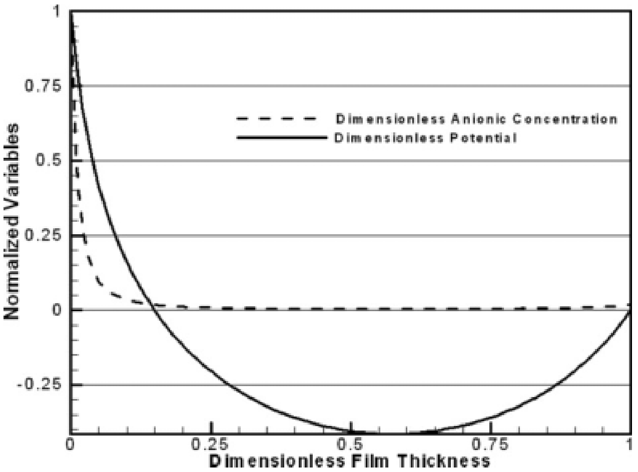

Figure 2. Analytically derived profile for very large time (equilibrium nature) for potential and entering anions (all normalized dimensionless forms) with respect to film thickness.

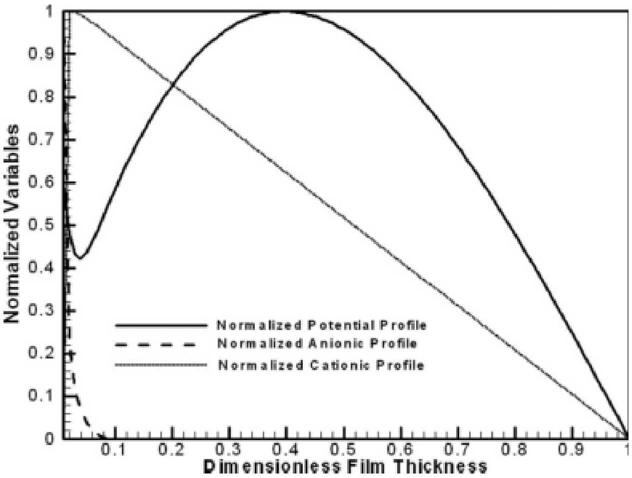

Figure 3. Numerically derived profile for initial time instance (t = 0.001 s), for cation, potential and entering anions (all normalized dimensionless forms) with respect to film thickness.

where $\alpha = \tan^{-1}\frac{\left(1-\frac{K.z^*}{2}\right)^{1/2}}{\left(\frac{K.z^*}{2}\right)^{1/2}}$ and $E_0^* = \ln\left(\frac{\cos^2\left(\alpha-\frac{K^{1/2}}{2}\right)}{\cos^2\,\alpha}\right)$. Constant K can be obtained from boundary condition on potential. The value as well as sign of K is decided by E^0 value at the interface.

Figure 2 shows the long time solution of potential and concentration of counter-ions inside the membrane by using Eq. 11 and 10, respectively. Counter-ions concentration deep inside membrane is order of magnitude smaller compared to concentration close to double layer interface though not exactly zero. Near surface there is a zone with sharply decreasing concentration. This is the ‘‘boundary layer.’’ Physically one does not expect a large excess charge to build up inside the membrane. Steady-state analysis shows that such excess charges would primarily depend on the anion concentration in the double layer in contact with the membrane and the potentials maintained at the two sides of the membrane by external means. Excess charges will be confined primarily to a thin boundary layer adjacent to the double layer as shown in Figure 2. High anion concentration maintained at the membrane surface tries to drive a large flux into the membrane. An excess charge therefore does build up inside the membrane, adjacent to the boundary, forming a ‘‘boundary layer’’ inside the polymer film. This excess charge produces a large electric field that opposes the concentration driven flux, virtually stopping it. In addition, the time required to build up this boundary layer is short. Also initially a very high gradient with respect to time exists, making the dynamic problem more stiff and difficult for numerical treatment (Figure 3). After a certain time period (Figure 4), inside the membrane and beyond the boundary layer, there will be three regions. The first one has very small excess of anion and second one is an incompletely neutralized zone, where there is still a little excess of cation. The third one waits for counter-ionic flux to come before getting neutralized and certainly, this region is also not electroneutral because of excess cationic charge not yet neutralized. The extent of the zone with little excess of cation depends on the reaction kinetic constants and for large values of those, the front will be very sharp, making the corresponding numerical problem very stiff. The scale of Figure 4 is, however, not sufficient to show these regions in details. From Figures 3 and 4, it is seen that beyond the boundary layer the concentration of the anions remains very small and apparently hardly changes with time. Actually, a very low concentration tongue (though not very noticeable at the scale of the figures) starts from the edge of the boundary layer and proceeds toward the opposite end. The shape of this tongue asymptotically approaches the steady-state profile shown in Figure 2. Since all numerical methods must start at time 0, and later on have a spatial boundary in the boundary layer, these steep gradient zones have to be dealt with care.

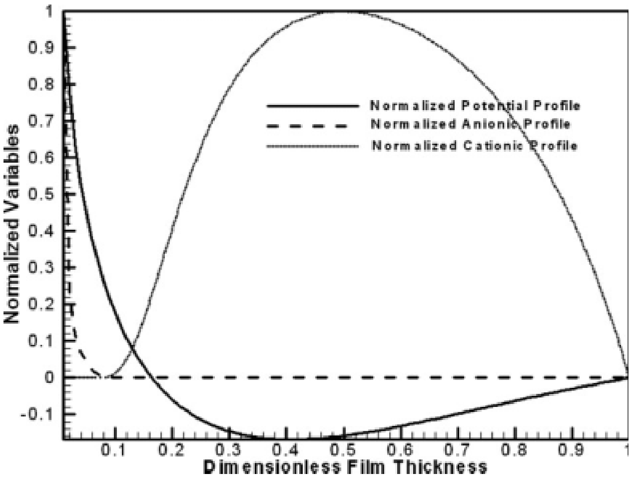

Figure 4. Numerically derived profiles at time = 10 s, for cation, potential and entering anions (all normalized dimensionless) forms with respect to film thickness.

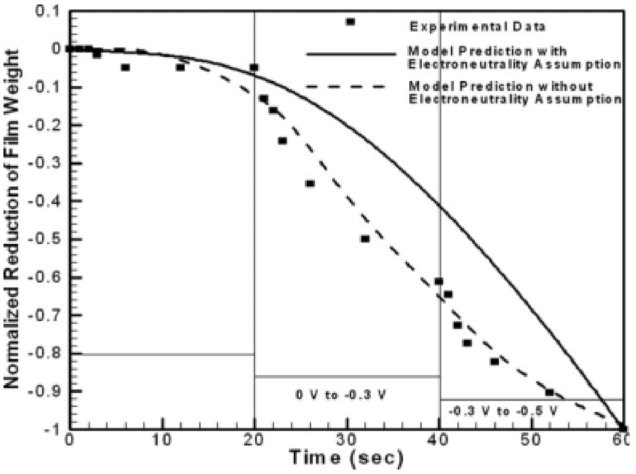

Figure 5. Comparison between the data of Kontturi et al.[15] and the simulation results (with and without electroneutrality assumption) for step-wise (voltage induced) release of molecules (voltage step changes have been shown in the figure) for a previously loaded CP film.

Small relative errors here will produce instability in numerical solution. At the end of the process (for very large *t*), there will be a very small excess of counterions, i.e., anions inside the membrane, but this excess will be orders of magnitude smaller than the concentration of counterions in the double layer (Figure 2). So the inside will be practically ‘‘electroneutral.’’ But a considerable excess charge will remain at the interface, in the boundary layer. The time scale required to reach such near electroneutral steady-state condition for the special class of system considered here is of the order of few tens to few thousand seconds. Such time scale depends on diffusivity, film thickness, concentration of cations inside the film, and anions in double-layer of the system. It has also been observed that the numerical routine has consistently solved for cases, where attainment of electroneutrality is much faster compared to the present case.

Model validations have been attempted against some available experimental studies in related areas. One such example is given here. Figure 5 shows the trend matching between simulation results and some of the experimental trends of Kontturi et al.[15] His experiment consisted of charging up a membrane with salicylate ions by application of a positive potential, then discharging the ions by application of negative potential applied in a stepwise manner. He presented the amount of discharge as a function of time, determined by EQCM study. It is assumed that all the change in mass is due to anion discharge. It should be noted, however, that only trends have been compared due to lack of necessary parameter data. Simulated results (without algebraic electroneutrality assumption case) closely resemble observed responses of the process. Case with electroneutrality assumption does not pick up the required sigmoidal trend in the experimental data especially after 20 s.

Finally, it appears that there has been no previous attempt to look into a critically important concept of electroneutrality for conducting polymeric solid porous electrodes. Unlike bulk liquid systems, the time scale of attainment of electroneutrality is much higher and it has been clearly shown that for this type of system, electroneutrality is not a justified assumption. A slight excess charge does build up, which causes a considerable change in the potential profile, as dictated by Poisson equation and this in turn limits ingress of ions into the films. This algorithm is capable of quantitatively explaining the ionic diffusion phenomenon, without the simplifying and unrealistic assumption of electroneutrality, and is uniformly applicable to both the boundary layer and the bulk of the film. This study shows that for precise control of drug delivery using CP-based electrodes, the effects of local charge accumulation and deviation from electroneutrality assumption need to be taken into account.

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