Compositional Gradients and Electron Flux in Ion-Blocked Multivalent Redox Polymers and Polymer Bilayers: A Theoretical Consideration

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Redox polymers that are both reducible and oxidizable can be driven to disproportionate when sufficiently large potential biases are applied across the polymer. Moreover, if the polymer is ionic in its original form, this disproportionation can be driven to occur without changes in the net ionic content of the polymer (the so-called ion-blocked case). In the first part of this paper we provide a theoretical description of the steady-state redox gradients that are established in ion-blocked multivalent redox polymers under voltage bias. In the second part of the paper a similar treatment is developed for ion-blocked redox polymer bilayers. The bilayer systems considered are ones in which the oxidation reaction is assumed to be sequestered entirely in one of the polymer layers and the reduction entirely in the other. The two types of polymer systems are compared. Also, comparisons are made between the predicted behavior under ion-blocked and non-ion-blocked conditions. Finally the potential advantages of bilayer polymers in applications such as solid-state electrochemically generated luminescence are discussed.

Introduction

So-called "electron-hopping" polymers are materials that contain high concentrations of *discrete* redox sites that are capable of undergoing reversible changes in the oxidation state.[1−6] When all of the redox sites are in a single oxidation state, the material is effectively an electronic insulator; however, when mixed-valent, it becomes an electronic conductor.[7−10] The mechanism of electron transport is electron exchange between adjacent sites in different oxidation states.[1,11−16] Typically, at least in the conducting mixed-valence form, such materials are ionic and require the incorporation of charge-compensating counterions to maintain electroneutrality. These counterions are generally mobile and electrochemically inactive.

For polymers that have only a single accessible redox process, such as polyvinylferrocene (i.e., 1+/0 couple for ferrocene), the single-valent material must undergo a net change in oxidation state (i.e., electrons must be injected into or removed from the polymer) in order for it to become conductive. Furthermore, since this process requires a *net* change in the polymer charge, the counterion content must also change to maintain charge balance. Once the material is rendered mixed-valent, however, the local oxidation-state composition can change without further changes in net ionic composition. For example, the application of a voltage bias across such a mixed-valent polymer can establish oxidation-state gradients without changing the net charge content.

When a polymer has more than one accessible redox couple, it may be possible to generate a locally mixed-valence material from a nominally pure oxidation-state form *without any net change in the ionic composition*.[17] If the pure valent form of a polymer can undergo a disproportionation, that reaction can be driven by a voltage bias just as it can in a simple solution electrochemical cell. Furthermore, the disproportionation can be accomplished in the polymer *without any net change in the*
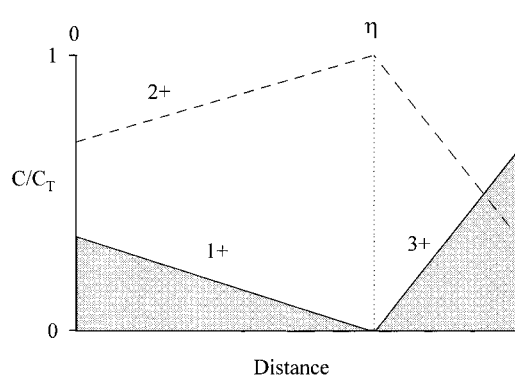

Figure 1. Plot of the redox site concentrations vs distance for a single ion-blocked polymer layer initially in the 2+ formal oxidation state. The results depicted are for the steady-state condition when the polymer is biased to drive the disproportionation reactions. The two shaded areas, which are equal, represent the quantity of charge transferred (across $x = \eta'$) between the regions containing the 3+/2+ and 2+/1+ gradients, respectively.

counterion content. In other words, $M^{1+} + M^{3+}$ and $2 M^{2+}$ each require 4 A^- for charge neutrality. The most prevalent chemical examples of multiple redox-couple polymers that can undergo voltage-driven disproportionations are poly-M(vb-py)$_3^{2+}$, where M is Fe, Ru, or Os and vbpy is 4-methyl-4′-vinyl-2,2′-bipyridine.[8,18−23]

When one of these materials is sandwiched between two metal electrodes and a voltage bias, ΔE, is applied that is approximately equal to the difference in the solution $E°$'s for the two couples, M^{2+} will be reduced at the cathode and oxidized at the anode. The counterion anions will redistribute themselves within the polymer to maintain local charge neutrality. At steady state the concentration profiles of redox states across the polymer will qualitatively resemble that shown in Figure 1 (vide infra). In general, the polymer will contain a region bounded between the cathode and $x = \eta$, which is composed of a gradient of M^{1+} and M^{2+}. Between η and the anode a

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second region composed of a gradient of M^{2+} and M^{3+} will exist. At the junction of these two regions, $x = \eta$, the comproportionation reaction between M^{3+} and M^{1+} occurs.

Recently, Murray, Wightman, and co-workers have demonstrated that these multi-redox-couple polymers can have properties that render them more than simple electrochemical curiosities.[22,23] For example, poly-Ru(vbpy)$_3$ and related materials exhibit steady-state electrochemiluminescence when biased so as to drive the $2Ru^{2+} \rightarrow Ru^{3+} + Ru^{1+}$ disproportionation. As part of these and earlier studies, steady-state concentration distance profiles for oxidation states of the sites within the polymer were described for two cases: (1) where the polymer is in contact with electrolyte solution and the potentials of the anode and cathode are each independently controlled with respect to a reference electrode (the "non-ion-blocked" case); and (2) where the polymer is dry or in contact with electrolyte-free solvent (or solvent vapor) and only the difference in potential between the anode and cathode is controlled (the "ion-blocked" case). These two cases differ in a number of respects, but most notably that in the former the net counterion composition of the polymer changes and in the latter it remains constant. The earlier theoretical treatment of the "non-ion-blocked" case has been adequate;[17] however, treatment of the "ion-blocked" case has not.[23] In some instances this has led to inaccurate pictures of the steady-state oxidation-state gradients extant within these materials.[23]

In what follows we present a theoretical consideration of the steady-state concentration distance profiles focusing on conditions where the total counterion content within the polymer remains fixed. Two cases are considered: The first consists of a single uniform multi-redox-couple polymer analogous to poly-Ru(vbpy)$_3^{2+}$. The second consists of a polymer bilayer in which the cathode reaction is entirely sequestered in one polymer and the anode reaction is sequestered in the other. These two systems have a number of common features and significant differences, which are underscored by their mutual consideration.

Ion-Blocked-Polymer Electron Flux

System 1: A Single Uniform Polymer Layer. Consider a single uniform polymer of thickness l sandwiched between a cathode located at $x = 0$ and an anode located at $x = l$. The redox site concentration, C_T, is assumed uniform throughout the polymer. In the absence of any potential bias, all of the redox sites are presumed initially in the $2+$ oxidation state. The counterions are assumed mobile, electrochemically inactive, and to have a $1-$ charge. The polymer is assumed to have $3+/2+$ and $2+/1+$ redox couples that are accessible and well separated in potential by an amount $\Delta E° = E°(3+/2+) - E°(2+/1+)$.

When a potential bias of approximately $\Delta E = \Delta E°$ is applied across the polymer, oxidation of $2+$ sites can ensue at the anode and reduction of $2+$ sites can ensue at the cathode. Since counterion transport in and out of the polymer is blocked, it follows from mass- and charge-balance that

$$\int_O^V C_3(x) \, dV = \int_O^V C_1(x) \, dV \tag{1a}$$

where $C_3(x)$ and $C_1(x)$ are the respective position-dependent concentrations of $1+$ and $3+$ sites and V is the polymer volume.

If it is assumed that the polymer is of uniform cross-sectional area, A, eq 1a becomes

$$A\int_O^l C_3(x) \, dx = A\int_O^l C_1(x) \, dx \tag{1b}$$

or

$$\int_O^l C_3(x) \, dx = \int_O^l C_1(x) \, dx \tag{1c}$$

Once a steady-state current is obtained, the redox site concentration gradients become constant with time. In general, the flux of electrons through any segment of the polymer will be governed by gradients in the redox site concentration (electron "diffusion") and electric fields within the polymer (electron "migration").[8,17,22,23] Up to the value of ΔE where the maximum redox site gradients allowed by the system constraints (vide infra) are achieved, there should be no electric fields within the bulk of the polymer (i.e., all of the potential drops should occur at the metal/polymer interfaces).[22,23] Consequently, only electron flux driven by redox site concentration gradients (electron "diffusion") should occur. Assuming only electron diffusion, it follows from Fick's law that

$$J_A = D_3\frac{dC_3}{dx}\Big|_{x=l} \tag{2a}$$

and

$$J_C = -D_1\frac{dC_1}{dx}\Big|_{x=0} \tag{2b}$$

where J_A and J_C are the fluxes of electrons across the anode/polymer and the cathode/polymer interfaces, respectively. D_3 and D_1 are the apparent electron-hopping diffusion coefficients in the regions of the polymer containing, respectively, the $3+/2+$ and the $2+/1+$ gradient. Since J_A and J_C must be equal by Kirchoff's law,

$$D_3\frac{dC_3}{dx}\Big|_{x=l} = -D_1\frac{dC_1}{dx}\Big|_{x=0} \tag{3a}$$

If the $3+/1+$ comproportionation constant is large, as it is for the poly-Ru(vbpy)$_3^{2+}$ case (because $\Delta E°$ is large), no significant amounts of $3+$ and $1+$ species will mutually exist within the same spatial region of the polymer assuming their reaction is fast. Thus, it follows that for $0 \leq x \leq \eta$ a region of pure $2+/1+$ gradient exists and $C_3(0 \leq x \leq \eta) = 0$. Similarly, it follows that for $\eta \leq x \leq l$ a region of pure $3+/2+$ gradient exists and $C_1(\eta \leq x \leq l) = 0$. Also, $C_2(\eta) = C_T$. Equation 1c thus becomes

$$\int_O^\eta C_1(x) \, dx = \int_\eta^l C_3(x) \, dx \tag{1d}$$

At steady state the oxidation-state gradient must be linear; consequently, eq 1d becomes

$$\frac{\eta C_1(0)}{2} = \frac{(l - \eta)C_3(l)}{2} \tag{1e}$$

and eq 3a becomes

$$D_1\frac{C_1(0)}{\eta} = D_3\frac{C_3(l)}{l - \eta} \tag{3b}$$

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Expressing the distance and concentration in unitless, fractional terms,

$$\frac{C_1(x)}{C_T} = C_1'(x) \tag{4a}$$

$$\frac{C_3(x)}{C_T} = C_3'(x) \tag{4b}$$

$$\frac{\eta}{l} = \eta' \tag{4c}$$

Substitution into eqs 1e and 3b yields

$$\eta' C_1'(0) = (1 - \eta') C_3'(l) \tag{5}$$

and

$$D_1 \frac{C_1'(0)}{\eta'} = D_3 \frac{C_3'(l)}{(1 - \eta')} \tag{6}$$

Equations 5 and 6 constitute the two main system constraints for an ion-blocked polymer under potential bias.

Recall that the potential difference between the anode and cathode is controlled externally, not their individual values. The Nernst equation gives

$$E_{anode} = E_{anode}^{\circ\prime} - \frac{RT}{nF} \ln\left(\frac{C_2'(l)}{C_3'(l)}\right) \tag{7a}$$

$$E_{cathode} = E_{cathode}^{\circ\prime} - \frac{RT}{nF} \ln\left(\frac{C_1'(0)}{C_2'(0)}\right) \tag{7b}$$

where the potentials are expressed relative to any arbitrary reference. For the case where $\Delta E = \Delta E^{\circ}$,

$$\Delta E = E_{anode} - E_{cathode} = E_{anode}^{\circ\prime} - E_{cathode}^{\circ\prime} \tag{8a}$$

Thus,

$$\frac{RT}{nF} \ln \frac{C_2'(l)}{C_3'(l)} = \frac{RT}{nF} \ln \frac{C_1'(0)}{C_2'(0)} \tag{8b}$$

or

$$\frac{C_2'(l)}{C_3'(l)} = \frac{C_1'(0)}{C_2'(0)} \tag{8c}$$

since $C_2'(l) = 1 - C_3'(l)$ and $C_2'(0) = 1 - C_1'(0)$, substitution and reorganization gives

$$(1 - C_3'(l))(1 - C_1'(0)) = (C_3'(l))(C_1'(0)) \tag{8d}$$

or

$$C_3'(l) + C_1'(0) = 1 \tag{8e}$$

Combining eqs 5 and 6, one obtains

$$\frac{C_1'(0)}{C_3'(l)} = \sqrt{\frac{D_3}{D_1}} = \frac{1 - \eta'}{\eta'} \tag{9}$$

Substituting eq 9 into eq 8e and solving for the surface concentrations gives

$$C_3'(l) = \frac{1}{1 + \sqrt{D_3/D_1}} \tag{10a}$$

$$C_1'(0) = \frac{\sqrt{D_3/D_1}}{1 + \sqrt{D_3/D_1}} \tag{10b}$$

As the bias, ΔE, is increased beyond $\Delta E = \Delta E^{\circ}$, each gradient becomes steeper until one of the two reaches its maximum value when either $C_1'(0)$ or $C_3'(l) \approx 1$. For still larger values of ΔE, the concentration of redox sites in the polymer will no longer be able to respond to the changes in ΔE; consequently, an electric field will develop within the polymer. Prior to reaching that value of bias voltage, the flux of electrons across the polymer will remain purely diffusional.[17]

It is instructive at this point to consider the situation where the diffusional flux is maximized. The quantity D_3/D_1 determines which of the two gradients reaches its maximum first. The maximum diffusional flux of electrons is determined as follows:

For $D_3/D_1 < 1$

$$C_3'(l) = 1$$

$$C_1'(0) = \frac{1 - \eta'}{\eta'}$$

For $D_3/D_1 > 1$

$$C_3'(l) = \frac{\eta'}{1 - \eta'}$$

$$C_1'(0) = 1$$

For $D_3/D_1 = 1$

$$C_1'(0) = C_3'(l) = 1$$

$$\eta' = 1/2$$

It should also be noted that the results of eq 9 are general and *independent of the bias voltage*, ΔE. Solving eq 9 for η' in terms of $\sqrt{D_3/D_1}$ gives[24]

$$\eta' = \frac{1}{1 + \sqrt{D_3/D_1}} \tag{11}$$

Figure 2 is a plot of η' vs D_3/D_1 (and $1 - \eta'$ vs D_1/D_3). Interestingly, η' (and $1 - \eta'$) are rather insensitive to the ratio of diffusion constants. The value of D_3/D_1 must deviate substantially from 1 for η' to move far from the center of the polymer. For example, when $D_3/D_1 = 10$, η' lies only approximately a quarter of the way across the polymer between the cathode and anode. When counterions are allowed to enter the polymer, a similar equation relating η' to D_3/D_1 exists which differs from eq 11 only in that the quantity D_3/D_1 is raised to the first power.[22,23] Consequently, η' is much *less* sensitive to relative differences in D_3 and D_1 when ion transport is blocked than when it is not.

Finally, Murray and co-workers demonstrated that upon sweeping the bias voltage, ΔE, applied across a solvent-swollen ion-blocked film of poly-[Os(bpy)$_2$(vpy)$_2$](ClO$_4$)$_2$ (where vpy = 4-vinylpyridine), a sigmoidal current−voltage curve re-
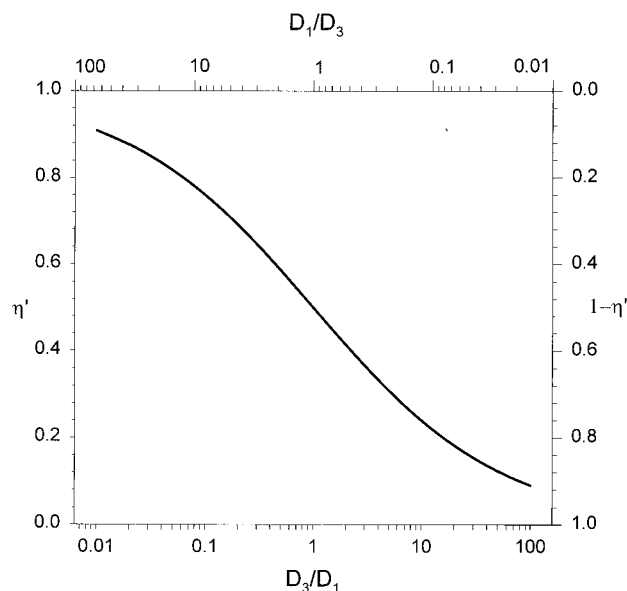
Figure 2. Plot of η' vs D_3/D_1 (and $1 - \eta'$ vs D_1/D_3) for an ion-blocked single polymer layer.

sulted.[17] At values of $\Delta E > \Delta E°$ (where again $\Delta E°$ is the separation in solution $E°$'s for the 3+/2+ and 2+/1+ couples) an approximately constant limiting current, i_l, resulted. Additionally, the value of ΔE corresponding to $i_l/2$ (the approximate analogue of $E_{1/2}$ in solution) occurred near $\Delta E°$. It is possible, from results derived herein, to entirely describe an idealized version of such a current−voltage curve. While such a full consideration is not undertaken here, the predicted behavior of ΔE at $i_l/2$ (hereafter $\Delta E_{1/2}$) as a function of D_3/D_1 is included because the results differ markedly from the non-ion-blocked case and from what might be intuitively anticipated. Only the results are given, but the derivations are straightforward. Two cases must be treated:

When $D_3/D_1 > 1$,

$$\Delta E_{1/2} = \Delta E° - \frac{RT}{nF}\ln(2\sqrt{D_3/D_1} - 1)$$

When $D_3/D_1 < 1$,

$$\Delta E_{1/2} = \Delta E° - \frac{RT}{nF}\ln(2\sqrt{D_1/D_3} - 1)$$

When $D_3 = D_1$ the two cases converge and $\Delta E_{1/2} = \Delta E°$. With solution voltammetry, $E_{1/2}$ shifts either positively or negatively relative to $E°$ depending on whether D_{OX}/D_{RED} is greater than or less than unity. For the ion-blocked polymer, $\Delta E_{1/2} \leq \Delta E°$ irrespective of which diffusion coefficient is the larger.

System 2: A Polymer Bilayer. Consider now a polymer bilayer of total thickness l, again sandwiched between a cathode at $x = 0$ and anode at $x = l$. Consider that this bilayer consists of two different polymers, P and Q. Polymer P, which contacts the cathode, is of thickness η, and polymer Q, in contact with the anode, is of thickness $(l - \eta)$. The concentration of redox sites in each polymer is assumed to be the same (i.e., $P_T = Q_T$). In the absence of any potential bias, ΔE, all sites are presumed again to be in their 2+ state. In contrast to the single polymer considered in system 1, the redox sites in polymer P are reducible only and the sites in polymer Q are oxidizible only. Finally, the two redox processes are again assumed to be well separated in potential (i.e., $E_P°(2+/1+) \ll E_Q°(3+/2+)$).

As with system 1, when the two electrodes are forward biased near $\Delta E°$, a reduction will occur at the cathode/polymer P interface, and an oxidation will occur at the anode/polymer Q interface. Furthermore, the system will in time reach steady state. A major phenomenological difference between the single polymer and the bilayer is that the boundary between the two polymers, η, also defines the boundary between the two types of redox gradients. Moreover, η is at a fixed position determined only by the relative thickness of the two layers.

Two types of system constraints analogous to eqs 3a and 1c apply to the bilayer.

$$D_{Q3}\frac{dQ_3(x)}{dx}\Big|_{x=l} = -D_{P1}\frac{dP_1(x)}{dx}\Big|_{x=0} \tag{12}$$

where D_{Q3} and D_{P1} are the apparent electron diffusion coefficients, respectively, along the 3+/2+ gradient in Q and along the 2+/1+ gradient in P.

And

$$\int_0^\eta P_1(x)\,dx = \int_\eta^l Q_3(x)\,dx \tag{13}$$

In contrast to the single-polymer case, there is no requirement for the bilayer that *both* $P_1(\eta)$ and $Q_3(\eta)$ be equal to zero; rather, it is sufficient that *either* $P_1(\eta)$ or $Q_3(\eta)$ equals zero. Again, it is useful to introduce unitless fractional concentrations and distance.

$$P_1' = P_1/P_T$$

$$P_2' = P_2/P_T$$

$$P_1' + P_2' = 1$$

$$Q_3' = Q_3/Q_T$$

$$Q_2' = Q_2/Q_T$$

$$Q_3' + Q_2' = 1$$

$$\eta' = \eta/l$$

Subsequently in the discussion, consideration will be limited to the condition of maximum possible diffusional flux.

It is instructive to consider initially the special case where η' is located such that

$$\sqrt{\frac{D_{Q3}}{D_{P1}}} = \frac{1 - \eta'}{\eta'}$$

When this condition is obtained, the steady-state redox site concentration gradients for the bilayer system are effectively identical to those that would occur for the single polymer (i.e., system 1) at all values of $\Delta E/\Delta E°$, namely, $P_1'(\eta) = Q_3'(\eta) = 0$. The only difference is that the two types of redox gradients remain sequestered within the two different polymers. In

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addition to this special case, there are four general cases that apply.

Case 1:

$$\sqrt{\frac{D_{Q3}}{D_{P1}}} > \frac{1-\eta'}{\eta'} \quad \text{and} \quad \eta' < \frac{1}{2}$$

Case 2:

$$\sqrt{\frac{D_{Q3}}{D_{P1}}} < \frac{1-\eta'}{\eta'} \quad \text{and} \quad \eta' < \frac{1}{2}$$

Case 3:

$$\sqrt{\frac{D_{Q3}}{D_{P1}}} < \frac{1-\eta'}{\eta'} \quad \text{and} \quad \eta' > \frac{1}{2}$$

Case 4:

$$\sqrt{\frac{D_{Q3}}{D_{P1}}} > \frac{1-\eta'}{\eta'} \quad \text{and} \quad \eta' > \frac{1}{2}$$

Cases 3 and 4 are mirror images of cases 1 and 2, respectively; that is, case 3 is obtained from case 1 by reversing $x = 0$ with $x = l$; consequently, further detailed discussion is limited to cases 1 and 2.

It is useful to first discuss the system constraints of eqs 12 and 13 in qualitative terms. In the absence of the constraint imposed by counterion mass- and charge-balance (i.e., eq 13), the maximum steady-state diffusional flux that could be obtained through each polymer layer *individually* would occur when that polymer segment becomes exactly half oxidized or half reduced (i.e., maximum mixed valency). Since the segments are in series, however, the maximum possible *total* flux would be limited by the smaller of these individual maximum fluxes. Thus, if

$$D_{Q3}/(1 - \eta') > D_{P1}/\eta'$$

then

$$P_1'(0) = 1 \quad \text{and} \quad P_1'(\eta) = 0$$

and the flux-limiting gradient occurs in the P polymer. If

$$D_{Q3}/(1 - \eta') < D_{P1}/\eta'$$

then

$$Q'_3(l) = 1 \quad \text{and} \quad Q_3'(\eta) = 0$$

and the flux-limiting gradient occurs in the Q polymer. Whether or not the mass- and charge-balance constraint will allow either of these individual maximum gradients to be achieved is determined by the relative values of $\sqrt{D_{Q3}/D_{P1}}$ and $(1 - \eta')/\eta'$ (vide infra).

Before considering results for these general cases, it is necessary to consider redox site gradients and interfacial concentrations accessible to a single polymer layer under three different conditions of overall redox level. For a given amount of injected charge (i.e., a net overall redox level), a continuous range of gradients is allowable. Figure 3 illustrates gradients of P_1' for three different oxidation levels: A, 33% (1+); B, 50% (1+), and C, 66% (1+). The dashed lines represent selected allowable steady-state gradients of 1+ sites. The solid
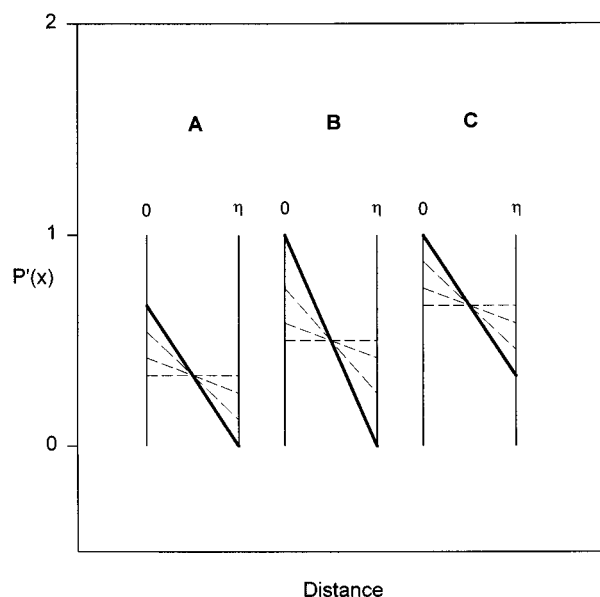

Figure 3. Concentration−distance profiles for the 1+ sites of a 1+/2+ mixed-valent polymer (analogous to polymer-P in text) at three different oxidation levels: (A) 33% 1+, 67% 2+; (B) 50% 1+, 50% 2+; (C) 67% 1+, 33% 2+. Each solid line represents the maximum 1+ site gradient possible for the respective oxidation level. The dashed lines represent selected allowed gradients less than that maximum.
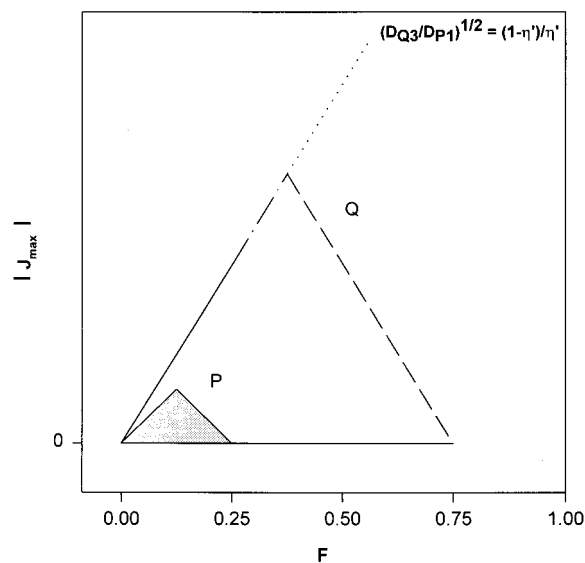

Figure 4. Plot of the maximum absolute electron diffusional flux across an ion-blocked bilayer polymer with $\eta' = 0.25$ as a function of F (see text for definition of F) for case 1. The shaded area represents allowable fluxes within the mass-balance constraints.

line depicts the *maximum* value of the gradient for that respective oxidation level. When the polymer is less than half reduced, the steepest gradient and maximum absolute flux, J_{max}, is obtained when $P_1'(\eta) = 0$. When the polymer is more than half reduced, J_{max} occurs when $P_1'(0) = 1$. Finally, the largest J_{max} possible is obtained when the polymer is exactly half reduced and occurs when $P_1'(0) = 1$ and $P_1'(\eta) = 0$. Therefore, for any given redox level, a continuous range of redox site gradients is possible, but there is a specific limit to the steepness. This maximum gradient, along with the electron diffusion coefficient, determines the range of diffusional fluxes, $J_{max} \geq J \geq -J_{max}$, allowable within the overall redox-state constraint.

Consider now Figures 4 and 5, which are plots of $|J_{max}|$ vs F, where $F_P = N_{P1}/N_T$ for P and $F_Q = N_{Q3}/N_T$ for Q. N_T is the
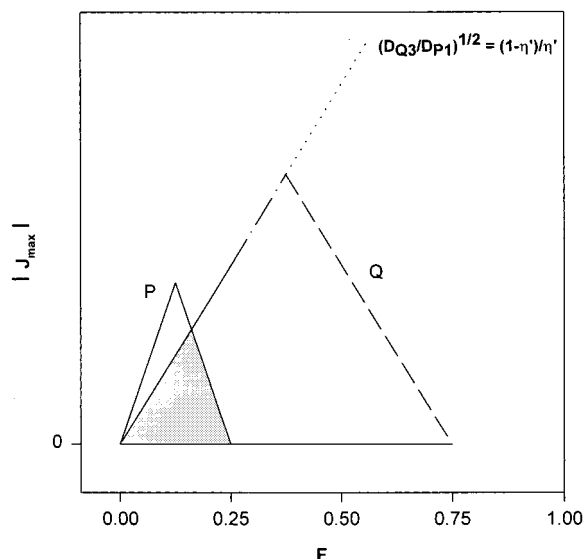
Figure 5. Same as Figure 4 for case 2.

total number of redox sites in the *entire* polymer bilayer, N_{P1} is the number of redox sites in P which are in the 1+ oxidation state, and N_{Q3} is the number of sites in Q which are in the 3+ oxidation state. The examples illustrated in Figures 4 and 5 are both for $\eta' = 0.25$. Charge-balance requires that $F_P = F_Q$; consequently, only the solid line portions of Figures 4 and 5 (i.e., $F \leq \eta' = 0.25$) are physically accessible. For $\eta' = 0.25$ P is completely reduced when $F_P = \eta' = 0.25$ and no more charge can be transferred to Q. Furthermore, $J_P = J_Q$; therefore only in the shaded regions of the figures (i.e., the region lying *below both curves where* $J \leq J_{max}$) can this condition be satisfied. The dotted line in each figure determines the boundary between case 1 and case 2 (i.e., $\sqrt{D_{Q3}/D_{P1}} = (1 - \eta')/\eta'$), such that if all of the P curve lies below this line, case 1 is obtained (Figure 4). If any part of the curve for the P polymer lies above this line, case 2 is obtained (Figure 5).

Consideration of Figures 4 and 5 provides insight into the conditions where the maximum possible $|J_{max}|$ occurs. In case 1, depicted by Figure 4, the entire P curve lies below the Q curve; consequently, the maximum allowable diffusional flux for a case 1 type bilayer occurs at J_{max} for P (i.e., when P is exactly 50% reduced). Thus, it follows that in case 1

$$P_1'(0) = 1$$

$$P_1'(\eta) = 0$$

$$0 < Q_3'(\eta) < Q_3'(l) < 1$$

For case 2, illustrated by Figure 5, the maximum allowable diffusional flux does not occur at the peak gradient for either polymer; rather it occurs at the peak of the shaded area. Furthermore, at this point P is more than 50% reduced (as is the situation in Figure 3C) and Q is less than 50% oxidized. Under those conditions, it follows that the maximum allowable diffusional flux occurs when

$$P_1'(0) = 1$$

$$P_1'(\eta) > 0$$

$$Q_3'(\eta) = 0$$

$$Q_3'(l) > 0$$

Recall that for large ΔE° the requirement exists that $P_1'(\eta)$ *or* $Q_3'(\eta)$ must be zero, and this condition is satisfied in each case. The consideration above provides two of the four concentrations ($P_1'(0)$, $P_1'(\eta)$, $Q_3'(\eta)$, and $Q_3'(l)$) needed to obtain the remaining two concentrations from eqs 12 and 13. The final result for each of the four cases is as follows.

Case 1:

$$P_1'(0) = 1$$

$$P_1'(\eta) = 0$$

$$Q_3'(\eta) = \frac{D_{Q3}(\eta')^2 - D_{P1}(1 - \eta')^2}{2D_{Q3}(1 - \eta')(\eta')}$$

$$Q_3'(l) = \frac{D_{Q3}(\eta')^2 + D_{P1}(1 - \eta')^2}{2D_{Q3}(1 - \eta')(\eta')}$$

Case 2:

$$P_1'(0) = 1$$

$$P_1'(\eta) = \frac{D_{P1}(1 - \eta')^2 - D_{Q3}(\eta')^2}{D_{Q3}(\eta')^2 + D_{P1}(1 - \eta')^2}$$

$$Q_3'(\eta) = 0$$

$$Q_3'(l) = \frac{2D_{P1}(1 - \eta')(\eta')}{D_{Q3}(\eta')^2 + D_{P1}(1 - \eta')^2}$$

Case 3:

$$P_1'(0) = \frac{D_{P1}(1 - \eta')^2 + D_{Q3}(\eta')^2}{2D_{P1}(1 - \eta')(\eta')}$$

$$P_1'(\eta) = \frac{D_{P1}(1 - \eta')^2 - D_{Q3}(\eta')^2}{2D_{P1}(1 - \eta')(\eta')}$$

$$Q_3'(\eta) = 0$$

$$Q_3'(l) = 1$$

Case 4:

$$P_1'(0) = \frac{2D_{Q3}(\eta')(1 - \eta')}{D_{Q3}(\eta')^2 + D_{P1}(1 - \eta')^2}$$

$$P_1'(\eta) = 0$$

$$Q_3'(\eta) = \frac{D_{Q3}(\eta')^2 - D_{P1}(1 - \eta')^2}{D_{Q3}(\eta')^2 + D_{P1}(1 - \eta')^2}$$

$$Q_3'(l) = 1$$

Discussion

Consideration of the results above brings to light a number of significant contrasts between the behavior of redox polymers when ion-blocked and when not. For the single polymer layer, the maximum diffusional flux will generally be lower when the counterion content of the polymer is fixed. Only when D_1/D_3

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= 1 are the two limiting diffusional fluxes the same. As the ratio of diffusion coefficients deviates from unity, the maximum diffusional flux for the ion-blocked polymer drops relative to that of the nonblocked case. For example, if the two diffusion coefficients differ by a factor of ×10, the maximum diffusion flux will differ by a factor of ca. 2.6. In the limit as the disparity between the diffusion coefficients becomes very large, the ratio of limiting fluxes approaches $\sqrt{D_3/D_1}$.
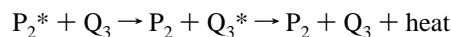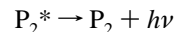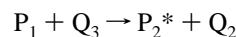
As demonstrated earlier for the case of an ion-blocked single polymer layer the position of the reaction layer is fixed at η. Moreover, η is independent of the voltage bias and determined only by the diffusion coefficients. The reaction layer can move within the polymer only if the net counterion content is allowed to change. When the potentials of the cathode and anode are independently controlled relative to an external electrode (which can only occur when ions move in and out of the polymer), the reaction layer can, in principle, be positioned anywhere within the polymer.

Comparison between the ion-blocked and non-ion-blocked polymer bilayer is slightly more complex than for the single polymer. The position of the reaction layer, η, is fixed by the structure of the polymer. Whether or not the maximum diffusion flux will respond to allowing the ion content of the polymer to change will depend on which of the four cases above is operative. For cases 1 and 3, the maximum redox site gradient has already been attained in one of the two layers (i.e., one segment is, on average, exactly 50% mixed-valent). Therefore, allowing the ion content of the polymer to change cannot increase the diffusional flux. In contrast, bilayers which fall into cases 2 or 4 cannot attain maximum gradients within either polymer segment while ion-blocked. Consequently, allowing the ion content of the polymer to change can increase the gradient in both polymer segments. The maximum diffusional flux will thus increase and ultimately be determined by the smaller of the possible limiting fluxes across the individual layers (i.e., much as in the situation with cases 1 and 3).

The boundary between the two types of polymers that comprise the bilayer can, in principle, be positioned anywhere within the polymer, including arbitrarily close to either the anode or cathode. Thus, a uniquely important feature of these bilayer polymers is the ability to control (via their physical construction) the position of the reaction layer independent of applied voltage, the values of the diffusion coefficients, and even whether or not the polymer is ion-blocked.

In contrast to the ion-blocked single polymer, it is only for the special cases where $\sqrt{D_{Q3}/D_{P1}} = (1 - \eta')/\eta$ that P_1 and Q_3 are both zero at η in a bilayer. Generally, either $P_1(\eta)$ or Q_3-(η) will be the limiting reagent and the other will be in excess. Unless the two diffusion coefficients are enormously disparate, moderate deviations of η' from 0.5 place the system well into case 2 (as $\eta' \rightarrow 0$) or case 4 (as $\eta' \rightarrow 1$). For example, when the two diffusion coefficients are the same and $\eta' = 0.1$, P is 98.8% reduced and Q is only 11.0% oxidized. Likewise, when $\eta' = 0.9$, Q is 98.8% oxidized and P is only 11.0% reduced. Also, whenever the diffusion coefficients are equal, reversing the thickness of the P and Q layers yields two bilayers having the *same* maximum diffusion flux (e.g., when $\eta' = 0.1$ and 0.9). Relaxing the assumption that $D_3 = D_1$ sacrifices the physical symmetry but does not negate the general results. While the maximum flux for two such bilayers would be the same, the concentrations of the individual redox levels at and near the reaction layer are quite different. To illustrate the possible ramifications of this observation, consider the circumstance where one of the reaction products at η is generated in a

luminescent excited state which, in addition, can undergo an energy-transfer quenching reaction with one of the two reactants. For example

$$P_1 + Q_3 \rightarrow P_2{}^* + Q_2$$

$$P_2{}^* \rightarrow P_2 + h\nu$$

$$P_2{}^* + Q_3 \rightarrow P_2 + Q_3{}^* \rightarrow P_2 + Q_3 + \text{heat}$$

In a bilayer, where the Q layer is thin, the concentration of Q_3 near η is high ($Q_3(\eta)) \rightarrow Q_T$ as $\eta \rightarrow 1$). However, by reversing the thickness of the two layers, the same diffusional flux results (assuming $D_3 = D_1$), but under conditions where Q_3 near η is small ($Q_3(\eta) \rightarrow 0$ as $\eta \rightarrow 0$).

Recall that the maximum diffusional flux for a P/Q-type bilayer is achieved when $\sqrt{D_{Q3}/D_{P1}} = (1 - \eta')/\eta'$. It follows that bilayers constructed with very different relative layer thickness are, in general, not optimized with respect to maximum diffusional flux. As a consequence, in the above example, constructing the bilayer with a thin P layer (small η') might be expected to improve the emission quantum yield by lowering the Q_3 concentration within the Föster radius[25] of η, but this would be accomplished at the cost of lowering the maximum diffusional flux. Recall also that bias voltage greater than that required to produce the maximum allowed redox site gradient produces electric fields within the polymer that increase the electron flux without concomitant changes in redox site gradients. Therefore, it does not necessarily follow that making the P layer thin reduces the current capacity of the bilayer. It simply increases the power consumption at a given current. Whether or not the light output characteristics would be improved (relative to, for example, a more flux-optimum bilayer structure) depends on the absolute light emissions of the two structures at a given power level.

Conclusion

Redox polymers that can be driven to disproportionate under a voltage bias behave quite differently depending on whether or not counterions are allowed to cross the polymer/solution interface. These differences are manifested in both the redox site gradients and electrode/polymer interfacial concentrations and are much more profound than has been previously indicated in the literature. Similar considerations extend to polymer bilayers that do not disproportionate but have chemically separate oxidation and reduction reactions sequestered, respectively, in the two polymer layers that comprise the bilayer.

Primarily for the sake of simplicity we have couched all of our discussions in the format of a specific set of fixed-site oxidation states, namely 3+, 2+, and 1+. These results are, nonetheless, general as long as the assumptions remain valid (e.g., $\Delta E°$ is large) and none of the oxidation states have formal charges that are of different signs. For example, the models developed herein would equally well apply to polymers having 2+/1+ and 1+/0 or 0/1− and 1−/2− redox couples, but they would not apply to a polymer (or polymer bilayer) which consisted of 1+/0 and 0/1− redox couples. Put another way, the polymer that is to be driven to disproportionate must initially be charged; otherwise, there are no counterions to redistribute under ion-blocked conditions. Moreover, this latter case has previously been treated under conditions where $\Delta E°$ is small and disproportionation of the neutral state is significant.[25]

Finally, bilayer polymers provide unique opportunities to exert control over an interfacial chemical reaction through the physical

construction of the polymer, a fact that is true irrespective of whether or not counterion content of the polymer is fixed.

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