# Charge Transport through Chemically Modified Electrodes: a General Analysis for Ion Exchange and Covalently Attached Redox Polymers

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The influence of physical diffusion of the electroactive species on the mechanism of charge transport in chemically modified electrodes is analyzed for ion exchange and covalently attached redox polymers with explicit consideration of vacant sites. The appropriate flux equation for charge transport is derived using phenomenological and probability considerations. The influence of both bounded and free physical diffusion rates on the charge transport dynamics is taken into account. The crucial role played by the physical displacement on "observables" such as effective diffusion coefficient, steady-state current, conductivity, transport number, mobility, etc., is demonstrated. The schematic variations of the above parameters on fractional loading and applied potential are shown for bounded and free diffusion conditions. The elucidation of physical displacement mechanism from the experimental response is indicated. The effect of solvent medium on the rate of charge transport is outlined using the formalism.

## 1. Introduction

The mechanistic analysis of charge transport in redox polymer electrodes is made difficult on account of several constituent interfacial processes such as

(i) physical diffusion of electroactive species within the polymer film, (ii) distance-dependent electron hopping between redox centers, (iii) movement of counterions in order to maintain electroneutrality, and (iv) polymer characteristics such as swelling, segregation, and partitioning.[1] Amidst such a scenario wherein several dynamical steps occur, it is but imperative that neither the precise choice of experimental techniques (transient vs steady state) nor a unified analysis globally valid is a priori possible. Consequently, a realistic strategy customarily employed in this context consists in the detailed study of the electron hopping process under diverse theoretical frameworks and experimental situations *in isolation*. A crucial preliminary step in this endeavor was the formulation of spatiotemporal diffusion migration equation for nearest-neighbor electron hopping by Savéant [2] via a bimolecular mechanism. This was also derived using thermodynamic[3] and irreversible thermodynamic approaches[4] apart from generalizations to include interactions between constituent redox species[5a] and long distance electron hopping.[6] However, the scheme of analysis of charge transport has been, in general, restricted to a detailed study of flux equation for electron hopping along with the concentration-dependent diffusion coefficient. The latter aspect, originally investigated by Dahms and Ruff et al. [7] for ionic solutions wherein electron exchange between reduced and oxidized species is taken into account, results in an apparent diffusion coefficient

$$D_{ap} = D_{phys} + \frac{k_{ex}\delta^2 C^\circ}{6} \qquad (1)$$

In the above equation, $D_{phys}$ is the diffusion coefficient for physical displacement of the redox molecules, $k_{ex}$ is the bimolecular rate constant for electron self-exchange, $C^\circ$ is the total concentration of the species, $\delta$ is the distance for electron hopping, and the factor 1/6 accounts for three-dimensional nature of the diffusion process. This equation enables the quantification of the rate constants of physical diffusion and electron exchange processes and is approximately valid for electrochemical processes occurring in bulk where charge transport is dominated by the physical diffusion of redox molecules. But in viscous media such as polymer matrix wherein the concentration of vacant sites can be varied over a wide range by careful experimental strategies, the rate of diffusion of redox species will show diverse patterns of behavior. Further, there is enhanced electron exchange between redox species, which increases its contribution to the observed diffusion coefficient. This effect was studied by Blauch and Savéant[8] using Monte Carlo simulation. This latter methodology despite its profound insight requires further improvization since the precise variation of the experimentally observed diffusion coefficient with respect to concentration of the electroactive centers is dependent upon (i) the nature of the redox polymer electrodes (polymeric system with covalently/electrostatically bounded redox centers), (ii) applied potential, and (iii) nature of interaction between the different charged species in the polymer.

The purpose of this paper is to (i) investigate phenomenological diffusion–migration equations for competitive physical displacement and electron hopping, (ii) propose a methodology for estimating the concentration of vacant sites in covalently attached and ion-exchange redox polymer electrodes, (iii) analyze the dependence of diffusion coefficients, steady state current response, conductivity, transport numbers, and redox capacity on system parameters, and (iv) propose the generalized Nernst–Einstein mobility relation for competing transport processes and (v) provide diagnostic criteria by which the occurrence of physical diffusion can be elucidated.

## 2. Model and Analysis

We consider the polymer as a three-dimensional network wherein the redox species are either covalently or electrostati-

cally bound. As a prototype of our analysis a redox couple (B/A) with charge $+2/+1$ and formal potential, $E^{\circ\prime} = 0.5$ V in the presence of a counterion (C) of charge $-1$, is assumed. Our formalism is applicable to both types of redox polymers, viz., (1) ion-exchange polymers in which the redox species are held by forces arising from electrostatic attraction and (2) polymers with covalently attached redox species. However, the calculation of vacancies is different for both the kind of polymers due to their different internal structures (cf. Appendix A). In redox polymers of the first kind[9] wherein ions like ferrocenium ion, $Co(bpy)_3^{3+/2+}$, etc. are incorporated in Nafion, polystyrene-sulfonate, the total volume of the film comprises that due to polymer, vacancies, and the redox species. Therefore, the volume occupied by the polymer should be excluded from the total film volume in the calculation of vacancy concentration. The mechanism of charge transport is also different in this case viz. on account of the electrostatic nature of the polymer−redox site bond, free as well as bounded diffusion of a redox species is possible depending on the bond strength.

On the other hand, in polymers of the second kind,[10] the monomeric redox species such as $Os(bpy)_3^{3+/2+}$, and $Os(bpy)_2$-$(vpy)_2^{3+/2+}$ are themselves electropolymerized and hence the total film volume is equal to the sum of the volumes occupied by the polymer (polymerized redox species) and vacancies. Also, due to the strong covalent bond existing between the redox centers and the polymer backbone, free diffusion of the redox centers is not possible. However, the redox species can move about their equilibrium point of attachment with the polymer, which is normally referred to as bounded diffusion. This bounded diffusion decreases the rate as well as the range of physical diffusion. The correlation effect arising from the nonrandom motion of the redox species also needs to be considered.[11] On account of this correlation, the displaced species has a higher probability to return back to its original position, thus reducing the net diffusion flux. Although we restrict ourselves to the one-dimensional flux equation, the exact values of the correlation factor for competitive diffusion processes in a bias (and sometimes time-dependent) potential are nontrivial. Consequently, we have assumed an approximate value for the correlation factor in our calculations. In the present analysis, we have excluded the effect of counterion diffusion and interaction between redox species since our objective is to decipher the influence of physical displacement on charge transport so as to infer its occurrence from the experimental response.

**2.1. Flux Equation.** In redox polymer electrodes, due to the viscous nature of the moiety, an important constituent process of charge transport is electron hopping between spatially separated redox centers. However, bounded or free physical diffusion of the redox species can also occur, which enhances the total charge transport rate. In such competing diffusion processes, the contribution of each flux toward the total charge transport needs to be considered. This is determined by the availability of occupied sites for electron hopping and vacant sites for physical diffusion. Thus, we write the total flux as

$$J_{\text{Total}}^{A} = \chi J_{\text{hop}}^{A} + f(1 - \chi)J_{\text{phys}}^{A} \qquad (2)$$

where $J_{\text{hop}}^{A}$ is the flux of the redox species A due to electron hopping and $J_{\text{phys}}^{A}$ refers to that for physical diffusion of the species under consideration, $f$ is the correlation factor which decreases the contribution of physical diffusion to the total flux, and $\chi$ denotes the fraction of occupied sites.

The individual electron hopping and physical diffusion fluxes are derived using simple probability considerations and the combined flux is given by

(cf. Appendix B)

$$J_{\text{Total}}^{A} =$$
$$-D_{\text{ap}}C_{\text{T}}\left\{\frac{\partial\chi_{\text{A}}}{\partial x} + \frac{F}{RT}\left[\chi_{\text{A}}z_{\text{A}} - \frac{D_{\text{hop}}}{D_{\text{ap}}}\chi_{\text{A}}(\chi_{\text{A}}z_{\text{A}} + \chi_{\text{B}}z_{\text{B}})\right]\frac{\partial\varphi}{\partial x}\right\} \quad (3)$$

where $\chi_{\text{A}}$ is the fractional concentration of reduced species (A) given as $C_{\text{A}}/C_{\text{T}}$, $\chi_{\text{B}}$ is that of the oxidized species (B) represented as $C_{\text{B}}/C_{\text{T}}$ within the film ($\chi_{\text{A}} + \chi_{\text{B}} = \chi$), and $C_{\text{T}} = C_{\text{A}} + C_{\text{B}} + C_{\text{V}}$. The above equation is applicable to both bounded and free diffusion conditions. In the analysis of Blauch and Savéant,[8] bounded diffusion is assumed to affect the charge transport only if electron hopping operates. However, in the analysis of the observables such as steady state current $I$, conductivity $\kappa_{\text{redox}}$, potential-dependent diffusion coefficient $D_{\text{ap}}(E_{\text{eq}})$, etc., this will lead to exclusion of bounded diffusion below and above the redox potential where electron hopping rate is negligible. Further, in the case of ion-exchange polymers bounded strongly to redox ions by means of electrostatic attractive forces, bounded diffusion varies with the solvent environment.[12] This will require explicit consideration of physical diffusion as regards its influence on the total flux (cf.. section 2.3).

When the rate of physical diffusion in a redox polymeric system becomes negligible ($D_{\text{phys}} \rightarrow 0$), the limiting form of eq 3, viz.

$$J_{\text{Total}}^{A} \approx -D_{\text{hop}}\chi\left\{\frac{\partial C_{\text{A}}}{\partial x} - \frac{nF}{RT}C_{\text{A}}\frac{C_{\text{B}}}{C^{\circ}}\frac{\partial\varphi}{\partial x}\right\} \qquad (4a)$$

that for electron hopping originally proposed by Savéant[2] is recovered when $\chi \rightarrow 1$. Analogously, when $D_{\text{hop}} \rightarrow 0$, eq 3 leads to

$$J_{\text{Total}}^{A} \approx -fD_{\text{phys}}(1 - \chi)\left\{\frac{\partial C_{\text{A}}}{\partial x} + \frac{Z_{\text{A}}C_{\text{A}}F}{RT}\frac{\partial\varphi}{\partial x}\right\} \qquad (4b)$$

which is identical with the classical Nernst−Planck equation when $\chi \rightarrow 0$.

**2.2. Diffusion Coefficient.** From the flux eq 3 for the competing diffusion process, we obtain the apparent diffusion coefficients for free and bounded diffusion as

$$D_{\text{ap}} = D_{\text{hop}}\chi + fD_{\text{phys}}(1 - \chi) \qquad (5)$$

where $D_{\text{hop}} = k_{\text{ex}}\delta^2 C^{\circ}/2$; $k_{\text{ex}}$ is the bimolecular self-exchange rate constant between nearest neighbors, $\delta$ is the distance for electron hopping, and $C^{\circ}$ is the total concentration of occupied sites.[13] $D_{\text{phys}} = k_{\text{phys}}\Delta\gamma^2/2$, where $k_{\text{phys}}$ is the rate constant for the unimolecular physical diffusion of the redox species and $\Delta\gamma^2$ is the corresponding mean squared displacement. The factor $^1/_2$ takes into account one-dimensional nature of the transport.

A few subtle features need to be pointed out here. In the study of redox polymer electrodes, the analysis and the solution of the diffusion−migration equation are considered exclusively assuming one-dimensional behavior whereas $D_{\text{ap}}$ is assumed to reflect the dimensionality (viz. $D_{\text{hop}} = k_{\text{ex}}\delta^2 C^{\circ}/6$ or $D_{\text{hop}} = k_{\text{ex}}\delta^2 C^{\circ}/4$). On account of the lack of information on precise estimates of rate constants, distances involved, and the number density of the redox centers, this discrepancy is not serious.

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However, the dimensionality plays a crucial role (i) regarding its variation with fractional loading in correlation factor and (ii) in percolation effects. The correlation factor has been alluded to earlier. As far as percolation is concerned, the following comments need to be made. Since polymer films are generally nonhomogeneous, consisting of several microstructures or domains within them,[14] the occurrence of percolation effects is a sine qua non. At low physical diffusion rates, these micro-clusters remain separated from each other and electron hopping, which is the predominant mode of charge transport under this condition, can take place only within each cluster. Such intracluster electron hopping is too low to be detected experimentally, whereby $D_{ap} = 0$ in this case (however, nonzero values of diffusion coefficient are observed in some experimental studies[15] which are explained on the basis of long distance electron hopping[6]). When the concentration of the occupied sites increases, the clusters come close to each other and at a particular concentration denoted customarily as the percolation threshold, a major cluster spans the entire system which can facilitate intercluster electron hopping. Therefore, above the percolation threshold the rate of electron hopping and hence that of charge transport increases rapidly. However, percolation thresholds, in general, should involve dependence on fractional loading, interaction schemes employed, and dimensionality of the system. In studies using chemically modified electrodes, the influence of the applied potential too needs to be analyzed. Since this is a formidable task, the percolation effects are neglected in our analysis, at present.

Another feature is concerned with the diffusion coefficient associated with physical displacement—the distance traveled by the species per diffusional jump will normally be greater than the edge-to-edge separation between the species, $\delta$, and we represent it as $\Delta\gamma$ so as to take into account the range of diffusion allowed by the polymer matrix. This variation in distance alone is often not adequate to influence the diffusion coefficient by orders of magnitude and the *frequency of jump* plays a central role in charge transport[16] and thus we differentiate between free diffusion and bounded diffusion in our analysis via a spectrum of values for $D_{phys}$, i.e., $D_{phys}$ ranging from $10^{-7}$ to $10^{-9}$ for free and $10^{-10}$ to $10^{-13}$ for bounded diffusion since the range of physical diffusion coefficient is found to vary from $10^{-8}$ to $10^{-13}$ cm$^2$ s$^{-1}$, depending upon the environment.[17]

The mechanistic aspects of charge transport can be understood from $D_{ap}$ vs $\chi$ plots. When the physical diffusion rate is low in the case of systems with bounded diffusion we obtain the limiting form of the observed diffusion coefficient as

$$D_{ap} = D_{hop}\chi = k_{ex}\delta^2\chi^2 C_T/2 \tag{6}$$

where $C_T$ is the total site concentration ($C_T = C_A + C_B + C_V$). Thus we obtain nonlinear variation of $D_{ap}$ with $\chi$, when the rate of physical diffusion is small.

If the rate of physical diffusion becomes larger than that of electron hopping rate, which can take place only in the case of free diffusion, the apparent diffusion coefficient becomes

$$D_{ap} = D_{phys}f(1 - \chi) \tag{7}$$

Accordingly, $D_{ap}$ should decrease with fractional loading.[18] This situation has its origin in the decreased availability of vacant sites for physical diffusion of the redox species. Figures 1 and 2 depict the variation of $D_{ap}$ with $\chi$ for free and bounded diffusion condition at different physical diffusion rates as estimated from eq 5.
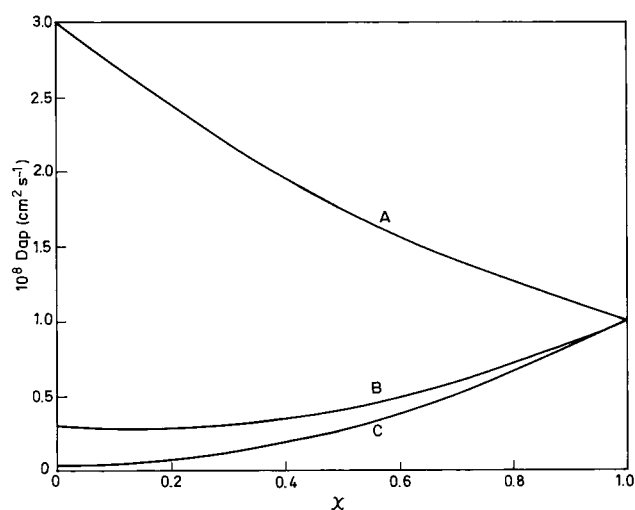


**Figure 1.** Variation of the apparent diffusion coefficient with fractional loading at $D_{phys}$ values (A) $1 \times 10^{-7}$, (B) $1 \times 10^{-8}$, and (C) $1 \times 10^{-9}$ cm$^2$ s$^{-1}$ calculated from eq 5.
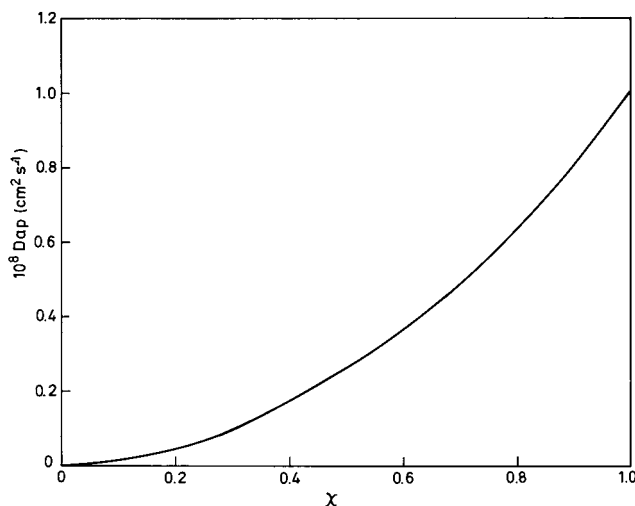


**Figure 2.** Variation of the apparent diffusion coefficient with fractional loading at $D_{phys}$ values $1 \times 10^{-10}$, $1 \times 10^{-11}$, and $1 \times 10^{-12}$ cm$^2$ s$^{-1}$. The three lines merge with each other, indicating that the exact magnitude of $D_{phys}$ does not alter $D_{app}$ in the case of bounded diffusion.

When both electron hopping and physical diffusion processes occur at the same rate, $D_{ap}$ becomes invariant with $\chi$[19] which can be obtained from eq 5 by applying the condition $D_{phys} = D_{hop}$ if we neglect the effect of correlations. However, in the case of systems with free diffusion, $D_{phys}$ is always higher. This promotes rapid reorganization of the clusters. Thus, intercluster electron hopping is plausible even at low fractional loading and percolation effect vanishes. Such a system is thus said to follow mean field behavior (absence of local correlations) for which $D_{ap}$ decreases with $\chi$, as discussed by Blauch and Savéant.[8] The percolation effect has been extensively discussed in the case of random resistor networks in various dimensionalities under different interaction schemes[20] (see also section 3).

**2.3. Solvent Effect on Diffusion.** The presence of solvent influences both electron exchange and physical diffusion, and let us first consider its effect on physical diffusion. Physical diffusion depends on the strength of the bond between the diffusing redox species and the coordinating center in the polymer, and when this bond is weak, diffusion becomes rapid. Nevertheless, the diffusion coefficient cannot approach the limit that is encountered in dilute solutions on account of the viscous nature of the polymer. Also solvent viscosity is related to the

diffusion coefficient by Stokes−Einstein law

$$D_{phys} = \frac{k_B T}{6\pi\eta r_h} \quad (8)$$

where $r_h$ is the hydrodynamic radius of the complex and $\eta$ is the viscosity of the solvent, $k_B$ being the Boltzmann constant. When an electrostatic bond between the redox ion and the polymer exists, solvents with increasing polarity will tend to weaken the bond and enhance physical diffusion whereas in the case of a covalent bond this effect is not very significant. The solvent effect has been considered for physical diffusion alone earlier[21] wherein solvent medium affects the activation energy for physical diffusion as,

$$k_{phys} = \frac{k_B T}{h} \exp\left(\frac{-\Delta G^{o\ddagger}{}_{phys}}{RT}\right) \quad (9)$$

$$\Delta G^{o\ddagger}_{phys} = W_r^e - W_m^e \quad (10)$$

$W_r^e$ and $W_m^e$ are the electrostatic free energies of an ionic species when it is present at the distance of closest approach r and an intermediate position m between two coordinating center of the polymer, respectively. The free energy at a distance $x$ wherein $r < x < l - r$ is given as

$$W_x^e = \frac{|z_F z_R|}{\epsilon} e^2\left(\frac{1}{x} - \frac{1}{l - x}\right) \quad (11)$$

$\epsilon$ being the permittivity of the solvent medium, $z_F$ and $z_R$ are the charges of the fixed site in the polymer and that of the redox species respectively, and $e$ is the electronic charge. These equations reflect the effect of solvated ionic radii, permittivity of the solvent, and charge of the ions on the physical diffusion rate. As the radius of the solvated ions increases, $W_r^e$ decreases, which leads to enhancement of the physical diffusion rate. Similarly, permittivity of the solvent has an inverse relationship with the activation energy, and hence its increase will enhance the rate of physical diffusion. Also as the charge of the ion increases, $k_{phys}$ increases. These effects are interrelated since solvents with higher relative permittivity can solvate the ions easily and increase the bare ionic radius. Similarly, cations with higher charge are solvated more. Thus increasing the amount of solvent as well as the order of the solvents from lower to higher polarity will increase the physical diffusion rate. The increase in conductance of the membrane with increase in water content is experimentally demonstrated for physical diffusion of mono-, di-, and tripositive metal cations in Nafion membrane.[21] This is due to the increase in the physical diffusion rate as well as changes in the microstructure of the film. When the solvent content decreases inside the film, ion pairing effect also becomes pronounced. Further, in solid-state voltammetric experiments with Nafion containing Os(bpy)$_3{}^{3+/2+}$ the rate constant for electron hopping is found to increase with relative humidity which can be explained as arising from the enhanced physical diffusion of the redox species associated with the water content within the polymer.[12] Since the polymer−redox species interaction[14b] is the cause of the observed order of physical diffusivity, it follows that the nature of the polymer also affects the diffusion of redox species. In fact, the diffusion behavior of thionine (TH$^+$) in polystyrenesulfonate (PSS) is similar to that observed in aqueous acidic solutions whereas that pertaining to Nafion is quite different. This is due to the different internal structures of PSS and Nafion. In PSS, the interior of the film is

hydrophilic whereas in Nafion it is composed of hydrophilic as well as hydrophobic parts. This is also reflected in the swelling factor, which is maximum for PSS film.

In the case of electron hopping, the self-exchange rate constant is given by Marcus equation as follows:[22]

$$k_{hop} = k_{pre}k_{el}\upsilon_n \exp\left[-\left(\frac{Ne^2}{16\pi\epsilon_0}\right)\left(\frac{1}{a} - \frac{1}{R_h}\right)\left(\frac{1}{\epsilon_{opt}} - \frac{1}{\epsilon_s}\right)\bigg/RT\right] \quad (12)$$

where $a$ is the equivalent reactant radius, $R_h$ denotes the inter nuclear separation of the reactants, $\epsilon_{opt}$ and $\epsilon_s$ are respectively the optical and static relative permittivities of the solvent, $k_{pre}$ is the equilibrium constant for forming the precursor (reactant pair) complex prior to electron transfer,[23] $k_{el}$ is the electronic transmission coefficient,[24] and $\upsilon_n$ describes the net dynamics along the nuclear reaction coordinate in the vicinity of the barrier top. Thus, the electron hopping rate constant decreases with increasing relative permittivity of the solvent.

Since we have demarcated the physical diffusion and electron hopping contribution terms separately for bounded and free physical diffusion, the solvent effect on the total observed rate can be studied for electrostatically attached redox species under both the conditions. If bounded diffusion influences the mean square displacement alone as assumed hitherto,[8] this insight cannot be obtained.

The effect of solvent in changing the microstructure of the film has been studied for [Os(bpy)$_2$Cl(PVP)](X)$_n$, bounded PVP film[25] wherein swelling of the polymer in the case of solvents with high polarity is reported. This is taken into account via the probability factor $(1 - \chi)$. As swelling occurs, the in situ thickness of the film increases and this leads to increase in concentration of vacancies as can be seen from the calculation reported in Appendix A. Thus, solvents of higher relative permittivity increases the contribution of physical diffusion to the total charge transport by increasing the rate as well as the probability of occurrence of physical displacement.

**2.4. Steady-State Current Response.** The experiments carried out under steady state conditions are especially suited to characterize charge transport in redox polymer electrodes since in steady-state experiments concentration gradient and potential gradient driven charge transport can be studied separately.[26] These experiments are normally performed for systems with bounded diffusion using sandwich or interdigitated array electrodes. The steady-state current response is given as

$$j = F\sum_{i=1}^{n} z_i J_i \quad (13)$$

where $i$ is the species index, $n$ denotes the electroactive species, and $j$ is the steady state current density.

*A. Concentration Gradient Driven Charge Transport.* Concentration gradient experiments are carried out using cells with two- or four-electrode geometry. The cross-exchange reaction between the redox species and the electrode is allowed to occur leading to the development of concentration gradient of the redox species within the film. Under this condition, potential gradient can be neglected since the diffusion of redox species and counterion movement lead to a reduction in the potential gradient. The steady state current density is given as

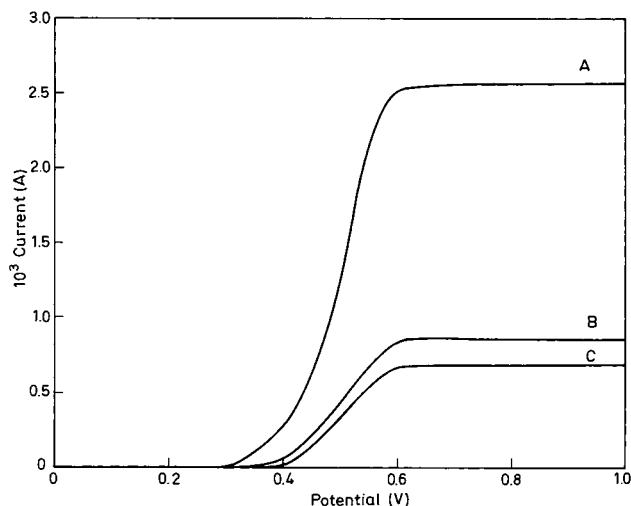$$j = -FD_{ap}\left\{z_A \frac{\partial C_A}{\partial x} + z_B \frac{\partial C_B}{\partial x}\right\} \quad (14)$$

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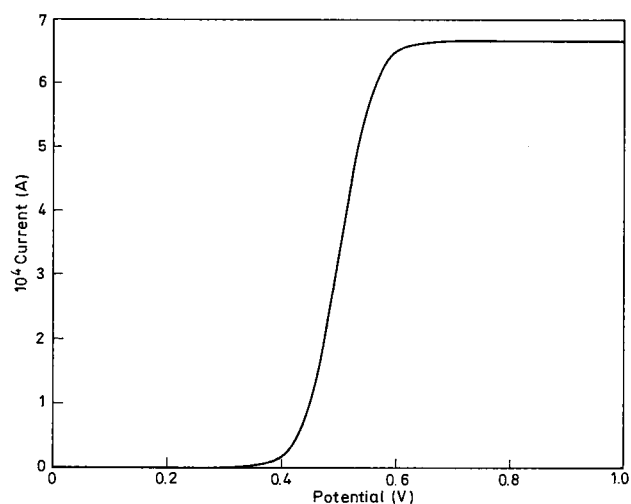**Figure 3.** Dependence of the steady-state current on applied potential ($\chi = 0.625$) at $D_{phys}$ values (A) $1 \times 10^{-7}$, (B) $1 \times 10^{-8}$, and (C) $1 \times 10^{-9}$ cm$^2$ s$^{-1}$ calculated from eq 15. In Figures 3−9, the formal potential $E^{\circ\prime}$ is kept as 0.5 V.



**Figure 4.** Dependence of the steady state current on applied potential ($\chi = 0.625$) at $D_{phys}$ values $1 \times 10^{-10}$, $1 \times 10^{-11}$, and $1 \times 10^{-12}$ cm$^2$ s$^{-1}$. All the three lines merge with each other, indicating that the steady state current does not vary with $D_{phys}$.

i.e.

$$j = nFD_{ap}\left\{\frac{\partial C_A}{\partial x}\right\} \tag{15}$$

where $n = z_B - z_A$ is the number of electrons transferred. We have calculated the concentration of the redox species at the electrode surface using Nernst equation. The limiting current is obtained from the above equation when the film comprises fully either the oxidant or reductant, i.e.

$$j_{lim} = nFD_{ap}\frac{C^{\circ}}{d} \tag{16}$$

In eq 16, $C^{\circ}$ is the total concentration of the occupied sites and $d$ is the thickness of the film. Since apparent diffusion coefficient depends on the nature of physical diffusion process (viz., bounded vs free), the variation of current density with applied potential can distinguish between the two kinds of physical diffusion. Figures 3 and 4 depict the steady-state current vs potential plots for free and bounded diffusion conditions at different $D_{phys}$ values. In the case of systems with free diffusion,
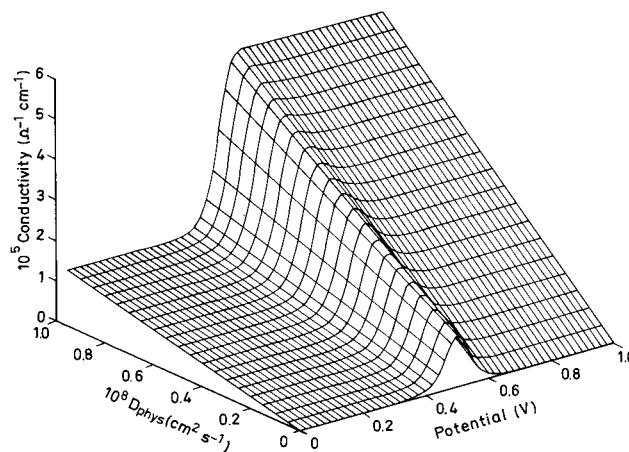


**Figure 5.** Variation of redox conductivity with applied potential and $D_{phys}$ values estimated from eq 18 when $\chi = 0.625$. The range of values chosen for the mesh plots are 0:0.025:1 for potential and $0.01 \times 10^{10}$:5 $\times 10^{-10}$:100 $\times 10^{-10}$ for $D_{phys}$.

the variation of current with $D_{phys}$ is large whereas for systems with bounded diffusion, steady state current−potential response is almost independent of $D_{phys}$ values.

*B. Potential Gradient Driven Charge Transport.* Potential gradient experiments are carried out using a two-electrode geometry. In these experiments counterion mobility is suppressed using various strategies, viz., (i) carrying out the experiment at low temperatures, (ii) employing high scan rate in potential sweep techniques, and (iii) using vapor-bathing environment. We note that counterion motion, if allowed, will facilitate cross-exchange reaction between the electrode and redox species so as to maintain charge neutrality, which leads to the development of concentration gradient within the film.[27] Hence it is suppressed. Consequently, the rate of physical diffusion of the species will also get reduced. However, bounded diffusion of the redox species can still take place, which contributes to charge transport within the film. Similarly, impedance spectroscopy can be used to obtain conductivity of the redox polymeric system.[28] However, conductivity for systems with free diffusion has not been reported hitherto. When the rate of counterion diffusion is low, the steady state current density for potential gradient driven charge transport is given as

$$j = -\kappa_{redox}\frac{\partial\varphi}{\partial x} \tag{17}$$

where

$$\kappa_{redox} = \frac{F^2 C_T}{RT}\{D_{ap}(\chi_A z_A^2 + \chi_B z_B^2) - D_{hop}(\chi_A z_A + \chi_B z_B)^2\} \tag{18}$$

$$D_{ap} = D_{hop}\chi + fD_{phys}(1 - \chi)$$

as in eq 5.

According to eq 18, the redox conductivity should increase with increasing physical diffusion rate due to the direct proportionality between redox conductivity and $D_{ap}$ (and in turn $D_{phys}$). Figure 5 shows the dependence of the redox conductivity on potential at different physical diffusion rates.

Under bounded diffusion conditions, the rate of physical diffusion is low; thus, electron hopping is the predominant mode of charge transport, which is characterized by nonohmic conductance. Conductivity increases with increase in fractional
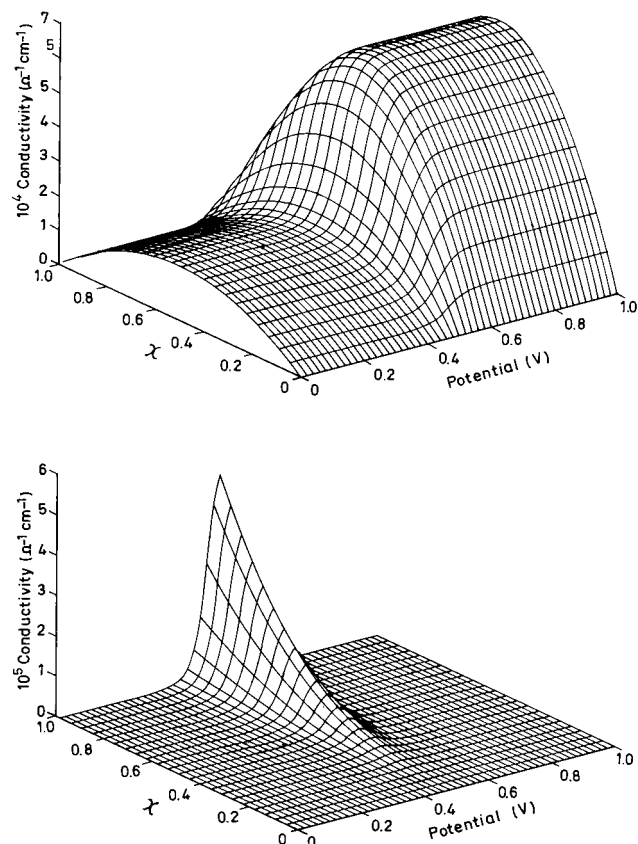
**Figure 6.** (a, top) Variation of redox conductivity with applied potential and fractional loading values for $D_{phys} = 1 \times 10^{-7}$ cm$^2$ s$^{-1}$. The range of values chosen for the mesh plots is 0:0.02:1 and 0:0.05:1 for potential and fractional loading, respectively. (b, bottom). Variation of redox conductivity with applied potential and fractional loading values for $D_{phys} = 1 \times 10^{-13}$ cm$^2$ s$^{-1}$. The range of values chosen for the mesh plots are 0:0.02:1 and 0:0.05:1 for potential and fractional loading, respectively.

loading in this limit. Figure 6, a and b, shows the variation of the redox conductivity with potential for various fractional loading under free physical diffusion and bounded diffusion conditions. As the physical diffusion rate increases, the redox conductivity changes from nonohmic to ohmic behavior (cf. Figure 5). Also when the physical diffusion rate becomes large, i.e., when $D_{phys} > 1 \times 10^{-10}$ cm$^2$ s$^{-1}$, redox conductivity increases with fractional loading initially due to increase in the charge carriers and decrease after a particular loading due to the blocking factor $(1 - \chi)$ (cf. Figure 6a); however, when the rate is very low such a variation is not seen (cf. Figure 6b) since electron hopping then becomes the favored mode of charge transport which increases with fractional loading continuously.

**2.5. Mediated Electron Transfer Reactions.** Electrocatalysis of solution phase reactant species by mediators incorporated in the polymer modified electrodes has been studied in several contexts such as fuel cells,[29] biosensors,[30] electroorganic synthesis,[31] etc. One of the main objectives of such anlaysis is the evaluation of rate constant for the cross-exchange reaction between the mediator and the reactant species. These experiments are normally carried out using redox polymer-coated rotating disk electrodes which yield the steady-state limiting current ($I_L$) through the Koutecky−Levich equation as

$$\frac{1}{I_L} = \frac{1}{I_E} + \frac{1}{I_K(1 - I_L/I_A)} \tag{19}$$

where $I_E$ is the current for charge transport within the film, $I_K$

is that for the cross exchange reaction between the mediator and the solution species, and $I_A$ refers to the current associated with the diffusion of the substrate in the bulk, when the reactant species is excluded from the polymer film on account of electrostatic repulsion. When $I_A$ is very large, the limiting current comprises the contributions from charge transport within the redox polymer and cross-exchange reaction, and both of them are independent of rotation speed ($I_E$ is also characterized by the independence of bulk concentration of the substrate). Thus the above analysis can be applied to study the kinetics of the cross-exchange process when $I_E$ is large. According to our formalism, the total flux of the mediator species within the redox polymeric system comprises contribution from the electron hopping as well as physical diffusion and, hence, the increase in $I_E$ in desired cases can be achieved by increasing the physical diffusion rate by means of solvent effect as discussed in section 2.3. However, it is imperative to consider solvent dynamics vis a vis dielectric constant effects on the cross-exchange rate constant in such studies.

**2.6. Transport Number.** The fraction of current carried by a redox species $i$ is given by

$$t_i = \frac{z_i J_i}{\sum_i z_i J_i} \tag{20}$$

Thus the transport numbers of reduced (A) species and oxidized (B) species in the absence of supporting electrolyte in the film are given as

$$t_A = \frac{D_{ap}\chi_A z_A{}^2 - D_{hop}\chi_A z_A(\chi_A z_A + \chi_B z_B)}{D_{ap}(\chi_A z_A{}^2 + \chi_B z_B{}^2) - D_{hop}(\chi_A z_A + \chi_B z_B)^2 + D_C z_C{}^2 \chi_C} \tag{21a}$$

$$t_B = \frac{D_{ap}\chi_B z_B{}^2 - D_{hop}\chi_B z_B(\chi_A z_A + \chi_B z_B)}{D_{ap}(\chi_A z_A{}^2 + \chi_B z_B{}^2) - D_{hop}(\chi_A z_A + \chi_B z_B)^2 + D_C z_C{}^2 \chi_C} \tag{21b}$$

where $D_c$ is the diffusion coefficient of counterion. If $t_{redox}$ is defined as[32]

$$t_{redox} = t_A + t_B$$

which is a measure of the charge transport within the film by both electron hopping and physical diffusion, we obtain

$$t_{redox} = $$
$$\frac{D_{ap}(\chi_A z_A{}^2 + \chi_B z_B{}^2) - D_{hop}(\chi_A z_A + \chi_B z_B)^2}{D_{ap}(\chi_A z_A{}^2 + \chi_B z_B{}^2) - D_{hop}(\chi_A z_A + \chi_B z_B)^2 + D_C z_C{}^2 \chi_C} \tag{22}$$

The transport number of counterions is given by

$$t_C = \frac{D_C z_C{}^2 \chi_C}{D_{ap}(\chi_A z_A{}^2 + \chi_B z_B{}^2) - D_{hop}(\chi_A z_A + \chi_B z_B)^2 + D_C z_C{}^2 \chi_C} \tag{23}$$

The measurement of $t_{redox}$ is not possible in steady state potential gradient experiments, since, as mentioned earlier, counterion transport is made to be negligible in such experiments and hence $t_{redox} \approx 1$. However, using impedance spectroscopy it is possible to distinguish mixed control (due to competitive diffusion and

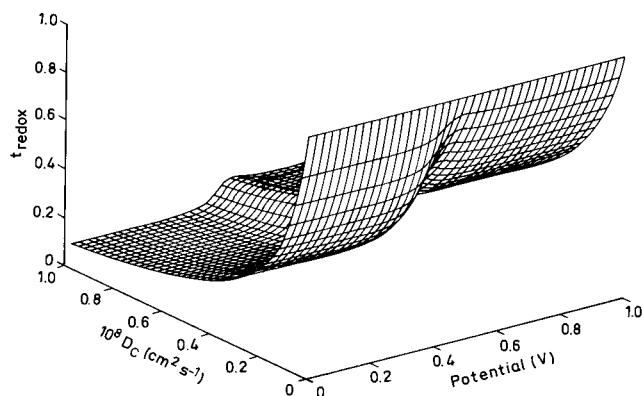Chemically Modified Electrodes

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**Figure 7.** Variation of $t_{redox}$ with applied potential and $D_c$ values for the fractional occupancy of 0.625 and $D_{phys}$ value of $1 \times 10^{-8}$ cm$^2$ s$^{-1}$ obtained from eq 22. The range of values chosen for the mesh plots is 0:0.025:1 for potential and $0.01 \times 10^{-10}$:$2.5 \times 10^{-10}$:$100 \times 10^{-10}$ for $D_c$ ($E^{\circ\prime} = 0.5$ V).

counterion mobility) from individual processes. This is achieved by the ratio of $R_{POL}/R_{LF}$ (=$3t_{redox}t_c$), where $R_{POL}$ is the resistance of the polymer and $R_{LF}$ is the low-frequency resistance.[25] This factor remains zero except under mixed control. However, we cannot isolate the individual transport numbers $t_{redox}$ and $t_c$. Figure 7 depicts the variation of redox transport number with the diffusion coefficient of the counterions. Under bounded diffusion conditions, transport is predominantly due to electron hopping and hence we observe a maximum in $t_{redox}$ at $E^{\circ\prime}$ whereas when physical diffusion dominates, $t_{redox}$ increases with potential and becomes constant when the rate of transport attains its maximum value. The variation in the plot of $t_c$ versus potential is complementary to that for $t_{redox}$, as expected.

**2.7. Redox Capacity and Diffusion Coefficient.** Redox capacity indicates the charge stored at equilibrium per unit volume for infinitesimal change of the potential relative to a reference electrode.[5]

$$\rho(E_{eq}) = dq/dE_{eq} \qquad (24)$$

where $q$ is the charge stored per unit volume (C cm$^{-3}$) and $E_{eq}$ is the equilibrium potential of the redox species in the presence of other species (such as counterions). It is given by

$$E_{eq} = -\frac{1}{F}\left(\mu_e + \frac{1}{z_C}\mu_C\right) + const \qquad (25)$$

$\mu_e$ and $\mu_c$ are the chemical potentials of the electrons (reduced species) and counterions, respectively.

$$dE_{eq} = -\frac{RT}{F}\left[\frac{\chi d\chi_A}{\chi_A(\chi - \chi_A)} + \frac{d\chi_A}{z_C^2\chi_C}\right] \qquad (26)$$

$$dq = -nFC_T\, d\chi_A \qquad (27)$$

If $n$ equals unity, we obtain

$$\rho(E_{eq}) = \frac{F^2C_T}{RT}\left[\frac{\chi}{\chi_A(\chi - \chi_A)} + \frac{1}{z_C^2\chi_C}\right]^{-1} \qquad (28)$$

Experimentally, redox capacity can be obtained from the measurement of the capacitance of the film whose volume is $V$, i.e.

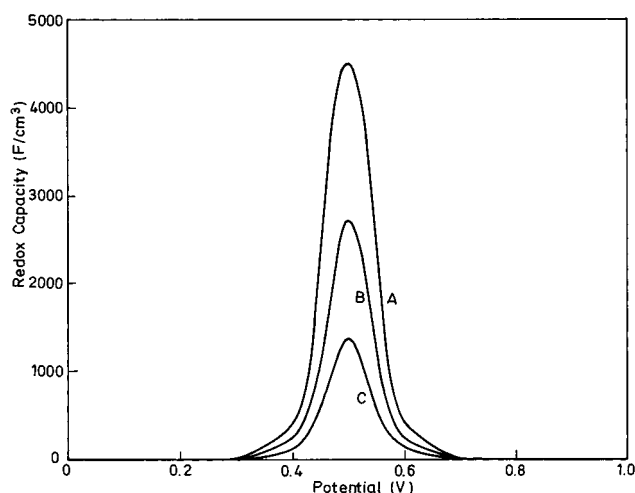$$\rho(E_{eq}) = C(E_{eq})/V \qquad (29)$$



**Figure 8.** Variation of redox capactiy with applied potential at fractional loadings (A) 1, (B) 0.6, and (C) 0.3 from eq 28.
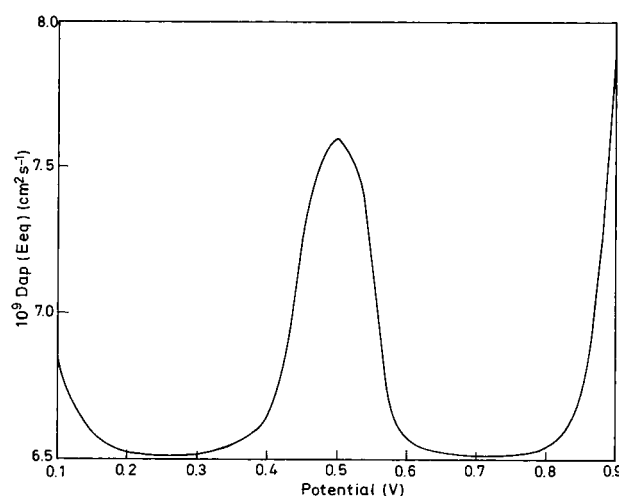


**Figure 9.** Variation of $D_{ap}(E_{eq})$ with applied potential for a fractional loading of 0.8 when $D_{phys} = 1 \times 10^{-15}$ cm$^2$ s$^{-1}$ from eq 31.

We analyze the effect of vacancies in the calculation of redox capacity neglected hitherto. The redox capacity increases with fractional loading (cf. Figure 8, but due to the blocking factor $\chi$, its magnitude is lower when compared to that obtained without its inclusion) and for each fractional occupancy, capacity maximum occurs at $E^{\circ\prime}$ where the rate of electron transport within the redox system is maximum thereby enhancing the electron transfer between the electrode and the redox polymeric system. From the ratio between conductivity and redox capacity, we deduce the potential dependent diffusion coefficient, i.e.

$$D_{ap}(E_{eq}) = \kappa_{redox}/\rho(E_{eq}) \qquad (30)$$

$$D_{ap}(E_{eq}) = [D_{ap}(\chi_A z_A^2 + \chi_B z_B^2) - D_{hop}(\chi_A z_A + \chi_B z_B)^2]$$
$$\left\{\frac{\chi}{\chi_A(\chi - \chi_A)} + \frac{1}{z_C^2\chi_C}\right\} \qquad (31)$$

If redox conductivity can be estimated for a system, eq 31 leads to $D_{ap}(E_{eq})$ values. But due to experimental constraints, $\kappa_{redox}$ has hitherto been obtained only for systems with bounded diffusion as discussed in section 2.5B. In such systems, $D_{ap}$-$(E_{eq})$ varies nonlinearly with potential. This is shown in Figure 9 in which the increase of $D_{ap}(E_{eq})$ at potentials far off from the formal potential of the redox couple is due to the effect of physical diffusion, which is maximum under such instances. If

**TABLE 1: Different Patterns of Experimental Behavior under Steady State Conditions and Their Rationalization Using the Formalism Given Here**

| exptl observables/ derived parameters | solvent characteristics | coupled diffusion (electron hopping coupled to counterion displacement) | competitive diffusion (electron hopping and physical displacement of redox species) |
|---|---|---|---|
| (A) observed diffusion coefficient | | $D_{ap} = D_{hop}\Psi_{LM}$, where $\Psi_{LM}$ is the dimensionless limiting current[42,38] | $D_{ap} = D_{hop}\chi + fD_{phys}(1 - \chi)$ |
| | solvents with high dielectric constants | $D_{ap}$ increases with $\chi$; its magnitude depends on the ion association constant | $D_{ap}$ decreases with $\chi$ due to physical diffusion control (cf. Figure 1) |
| | solvents with low dielectric constants | | $D_{ap}$ increases with $\chi$ due to electron hopping being predominant (cf. eq 6 and Figure 2) |
| (B) steady state current | | | |
| (i) concentration gradient experiment | solvents with high dielectric constants | no appreciable solvent effect since it has opposite effects on the rate of electron hopping and the availability of the dissociated electroactive species | increases with every 10-fold increase in $D_{phys}$ (cf. Figure 3) |
| | solvents with low dielectric constants | | invariant with Dphys (cf. Figure 4) |
| (ii) conductivity | solvents with low dielectric constants | non-ohmic conductivity | non-ohmic conductivity (cf. Figure 6b) |
| | solvents with high dielectric constants | ohmic conductivity of lower magnitude,[32] provided $D_c$ is not affected by solvent | ohmic conductivity of higher magnitude (cf. Figure 6a) |
| (C) transport number | | $t_e$ (transport of number of electron) can vary between 0 and 1 when physical diffusion of the redox species is neglected | $t_{redox}$ cannot approach unity since $D_c$ is normally greater than $D_{phys}$ (cf. Figure 7) |

the rate of physical diffusion increases, then $D_{ap}$ becomes invariant with potential.[33] Thus, the $D_{ap}(E_{eq})$−potential plots can indicate the influence of physical diffusion on the total charge transport rate.

**2.8. Combined Mobility for Physical Diffusion and Electron Hopping.** It is possible to derive the mobility equation for the competing transport process starting from the flux eq 3 since mobility of an electroactive species $i$ is the mean velocity under unit potential gradient

$$u_i = -\frac{J_i}{C_i(\partial\varphi/\partial x)} \quad (32)$$

Further,[34] the specific conductivity is expressed as

$$\kappa = F\sum_{i=1}C_iz_iu_i \quad (33)$$

where the summation index is over all the species and

$$\kappa_i = C_iz_iu_iF \quad (34)$$

or analogously

$$\kappa_i = -\frac{z_iJ_iF}{\partial\varphi/\partial x} \quad (35)$$

from which we obtain eq 32. Thus, the mobility of the reduced species A due to both electron hopping and physical diffusion can be written as

$$u_A = -\frac{J_{Total}^A}{C_A(\partial\varphi/\partial x)} \quad (36)$$

Substituting for $J_{Total}^A$ from eq 3 we obtain

$$u_A = \frac{D_{ap}F}{RT}\left[z_A - \frac{D_{hop}}{D_{ap}}(\chi_Az_A + \chi_Bz_B)\right] \quad (37)$$

We may note that when $D_{hop} \to 0$ and the number of vacant sites is large (i.e., $\chi \to 0$, when $f$ becomes unity[35]), the Nernst−Einstein mobility relationship

$$(u_A)_{phys} = z_AFD_{phys}/RT \quad (38)$$

is obtained. Analogously, when $D_{phys} \to 0$ and the concentration of occupied sites is large (i.e., $\chi \to 1$), we obtain the mobility of A arising from the electron hopping process

$$(u_A)_{hop} = -\frac{nFD_{hop}}{RT}\frac{C_B}{C^\circ} \quad (39)$$

The negative sign accounts for the electronic charge since $u_A = u_e$, A being the electron donor. Thus, for competitive diffusion, the total mobility of a species A due to two different processes is a weighted arithmetic mean, viz.

$$u_A = \chi(u_A)_{hop} + f(1 - \chi)(u_A)_{phys} \quad (40)$$

when $\chi = C^\circ/C_T$ and $\chi_B = C_B/C_T$.

**3. Perspectives**

The foregoing analysis has provided a simple framework whereby the influence of physical diffusion on the observed charge transport rate can be deciphered. Though steady state potential gradient experiments can be performed only to characterize systems with bounded diffusion, the effect of physical diffusion can no longer be ignored in the case of concentration gradient driven experiments (steady state or transient). Even in the case of systems with bounded diffusion, the effect of physical diffusion is significant as demonstrated here. The flux is derived for a one-dimensional case since the incorporation of higher dimensions is not expected to alter most of the qualitative features of the schematic variations represented here. The essential feature of the formalism consists in distinguishing the behaviors of ion-exchange polymers and covalently attached polymers as regards the role of physical diffusion. Table 1 provides the scheme by which the influence of physical diffussion can be deciphered from experimental response.

The methodology for calculating the concentration of vacant sites in the polymer moiety is provided for ion-exchange and covalent polymers. Although the nontrivial nature of the vacancy effects was recognized earlier,[8] what marks the present analysis as different is the incorporation of these considerations into the formalism for flux equation. This is especially crucial if our objective is to solve diffusion equations pertaining to potential step or potential scan experiments for redox polymeric systems. This would involve per force numerical approaches, which will

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lead to the construction of working curves for diagnostic purposes. We may note that the linearity between (i) $I$ and $\nu^{1/2}$ and (ii) $I$ and $\nu$ (where $\nu$ is the scan rate in cyclic voltammetry) is taken as the criterion for the elucidation of the mechanism of electrochemical reactions. Further, such plots or their variants are employed to obtain the concentration of redox centers, film thickness, diffusion coefficient, etc. in electrocatalysis involving chemically modified electrodes. The analysis expounded here would provide a basis by which the experimentally observed response can be delineated in terms of polymer characteristics, rate controlling process in charge transport, viz. electron hopping, physical diffusion, etc.

Although the formalism of flux equations reported here can be accomplished by other methods based on kinetic Ising model formalism,[35] irreversible thermodynamic versions, chemical kinetic schemes, etc., our emphasis consists in obtaining system parameters such as redox capacity, transport number, conductivity, etc. from the flux equation so that hierarchical improvements to the present framework is feasible. For example, the incorporation of activity coefficient effects, interparticle interactions, partitioning behaviors, polymer characteristics, and precise time constants needs to be carried out in order to provide a comprehensive approach. However, this study provides a scheme by which these effects can be studied further at least on phenomenological grounds. A limitation of the present approach is the qualitative manner in which correlation factor is introduced. This is at present unavoidable, since a correct analysis of this procedure would require a many-body theory involving two competing transport processes and "closure assumptions" to solve Green's function of the system characterizing the movement of charged species. Consequently, the value of the correlation factor is assumed in an ad hoc manner. This limitation, along with the unavailability of precise estimates for $\Delta\gamma^2$, needs to be pointed out here. In fact, $\Delta\gamma^2$ are themselves dependent upon the number density vis a vis film thickness as shown elsewhere.[36] If this feature is taken into account, we believe that all types of variations pertaining to diffusion coefficient, redox capacity, conductivity, etc. can be qualitatively rationalized.

The effect of physical diffusion of redox species has been explained in several contexts assuming single file diffusion.[37] The difference in the variation of the observed diffusion coefficient patterns ($D_{2/3}$ and $D_{2/1}$) of $[Co(bpy)_3]^{3+/2+}$ and $[Co(bpy)_3]^{2+/+}$, respectively, with the concentration of $[Co(bpy)_3]^{2+}$ has been explained by assuming the partition coefficient as well as diffusion coefficient of the redox species to be different in various clusters of the polymer. However, the contribution of physical displacement and electron diffusion coefficient has not been isolated in each of the clusters. Our formalism is applicable to such a system where the decrease of $D_{2/3}$ and increase of $D_{2/1}$ with the concentration of $[Co(bpy)_3]^{2+}$ can be understood on the basis of the changes in the rate of electron hopping for reduction and oxidation and the subsequent counterion intake or exclusion which modifies the interaction between the loaded redox species and the polymer; thus $D_{hop}$ as well as $D_{phys}$ estimates are affected under different experimental conditions (oxidation/reduction) thereby altering $D_{ap}$. However, the present framework is also applicable to systems where even in the absence of such clusters, this type of experimental behavior is noticed.

We have excluded the effect of counterion displacement from our analysis assuming that it essentially influences charge transport by modifying the polymeric structure or by ion pairing.[38] A detailed study incorporating counterion mobility

into the flux equation may make the analysis more cumbersome, but will be a desirable pursuit.

## 4. Summary

The contribution of physical diffusion of redox species to the total charge transport within the polymer film is considered for formulating spatio-temporal flux equations, and the results for apparent diffusion coefficient for free physical displacement and bounded diffusion are derived. The equations for steady state current, conductivity, redox capacity, and mobility are derived, and the dependence of these parameters on fractional loading and applied potential is schematically depicted. The effect of vacant sites and physical diffusion rate on these parameters is discussed for both bounded and free physical diffusion conditions. The qualitative influence of solvent medium on the apparent diffusion coefficient is pointed out.

## Appendix A

**Calculation of Vacancy Concentration in Redox Polymer Electrodes.** The volume of the film (coated on to the electrode surface) consists of that due to the polymer, redox ions, and vacancies. The concentration of the individual constituents can be estimated from their respective volume fractions. As mentioned in the text, we need to incorporate the different internal structures of the polymers in the calculation.

In polymers of second kind, viz. poly$[Os(bpy)_2(vpy)_2]^{3+/2+}$ where the redox ion $[Os(bpy)_2(vpy)_2]^{3+/2+}$ is itself the monomeric species which is later electropolymerized, the redox species constitutes a part of the polymeric structure. In this case, the total film volume ($V_T$) is the sum of the volume of the redox species ($V_R$) (polymer) and vacancies ($V_V$). The total film volume is calculated from the area and thickness.[39] Since in experimental studies the reliable value for area is not reported, the area of the electrode is assumed to be equal to the area of the film. Further, wet thickness of the film should be used in the calculation, which is normally not available. Due to these two restrictions, a direct comparison of our calculation with experimental data is precluded.

Let $V_T$ be the total volume of the film.[40] The volume occupied by each species is $v_i$ (equals $8R^3$ in the case of cubic lattice if $2R$ is the diameter of the ion). From the value of $\Gamma^\circ$ which represents monolayer coverage of the film, calculated from experimental data and from the wet thickness of the film ($d$), the concentration of the redox ion inside the film may be estimated. The total volume occupied by the redox species in the film then follows as

$$V_R = v_i C^\circ N_A V_T \tag{A-1}$$

$N_A$ being the Avogadro number and $V_T = V_V + V_R$. The concentration of vacancies is

$$C_V = \frac{C^\circ}{V_R}(V_T - V_R) \tag{A-2}$$

Our calculation of the total site concentration ($C_T = C_V + C^\circ$) gives a result identical with that reported earlier,[8] since both treatments assume the redox species to occupy a cubic lattice.

For ion-exchange polymers, with incorporated redox species, e.g., Nafion film containing $Cp_2FeTMA^{+/0}$, the total film volume consists of that occupied by the polymer, redox species, and vacancies since here the redox species are not part of the polymer matrix. The film volume ($V_T$) and the total volume

occupied by the redox species ($V_R$) are calculated as earlier. But $V_T = V_P + V_V + V_R$, where $V_P$ is the volume of the polymer and $V_V$ is that of the vacancies. If the weight of the coated polymer is $W_P$, the volume occupied by the polymer in the film can be calculated from its dry density $\rho_P$ since

$$V_P = W_P/\rho_P \qquad (A\text{-}3)$$

The volume of the vacancy ($V_V$) can be subsequently converted into its concentration ($C_V$) as described above and the total site concentration is given as $C_T = C° + C_V$. If the weight of the loaded polymer is not precisely known, the concentration of the polymer can be obtained by knowing its equivalent weight ($E_W$), since

$$C_P = \rho_P/E_W \qquad (A\text{-}4)$$

The total concentration of the polymer and vacancy is

$$C_P + C_V = \frac{C°}{V_R}[V_T - V_R] \qquad (A\text{-}5)$$

wherefrom $C_V$ is obtained. Equations A-2 and A-5 provide, respectively, the method of estimating vacancy concentration in the case of covalent and ion-exchange polymers. Since we have estimated the relative volume of vacancies so as to obtain their concentration, the consideration of effective volume through which the redox species can diffuse (which is customarily carried out in the study of diffusion in polymer matrices[16]) is not required.

## Appendix B

**Flux Equation for Electron Hopping and Physical Displacement.** We follow the procedure advocated by Chidsey and Murray[5a] for the derivation of flux equation; however, we introduce a few subtle variations, viz., (i) we consider the polymer as a macroscopic network within which redox sites and vacancies are uniformly distributed such that the system is stable, and diffusion by both the processes in a particular direction can be described by that between adjacent sites; (ii) we consider edge-to-edge separation to describe the electron hopping distance instead of the lattice parameter. Thus, the ambiguity in illustrating the difference between[5a] edge-to-edge and center-to-center distance in the electron hopping diffusion coefficient is overcome.

Consider the nearest-neighbor electron hopping which can be represented as

$$A_1 + B_2 \overset{k_{ex}}{\rightleftharpoons} A_2 + B_1 \qquad (B\text{-}1)$$
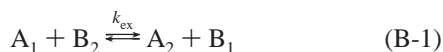
where 1 and 2 represent the indices of the adjacent sites separated by electron hopping distance $\delta$. The flux of A between the sites 1 and 2 due to electron hopping is given as

$$(\vec{J}_A)_{hop} = {}^1\!/_2 \delta \vartheta_{AB}(1 + \xi)C_{A,1}C_{B,2} \qquad (B\text{-}2a)$$

$$(\overset{\leftarrow}{J}_A)_{hop} = {}^1\!/_2 \delta \vartheta_{AB}(1 - \xi)C_{A,2}C_{B,1} \qquad (B\text{-}2b)$$

where $^1/_2$ accounts for the one-dimensional nature of the process. $\vartheta_{AB}$ is the jump frequency, $\xi$ is the dimensionless force arising

from the applied electric field given as $\xi_{hop} = \pm(nF\delta/2RT)(\partial\varphi/\partial x)$ under low potential gradient and depends on the direction of the applied field. The net flux of A in the forward direction is

$$J^A_{hop} = (\vec{J}_A)_{hop} - (\overset{\leftarrow}{J}_A)_{hop} \qquad (B\text{-}3)$$

$$J^A_{hop} = {}^1\!/_2 \delta \vartheta_{AB}(1 + \xi_{hop})C_{A,1}C_{B,2} - {}^1\!/_2 \delta \vartheta_{AB}(1 - \xi_{hop})C_{A,2}C_{B,1} \qquad (B\text{-}4)$$

In eq B-4, the expansion of the concentration terms using the Taylor series is carried out and terms higher than the second order are ignored. On application of Gibbs−Duhem equation and the constraint that the concentration of vacancies is constant, we obtain

$$J^A_{hop} = {}^1\!/_2 \delta^2 \vartheta_{AB} \frac{C_A C_B}{RT}\left[\frac{RT}{C_B}\frac{\partial C_B}{\partial x} - \frac{RT}{C_A}\frac{\partial C_A}{\partial x} + nF\frac{\partial\varphi}{\partial x}\right] \qquad (B\text{-}5)$$

The above equation (B-5) becomes consistent with that reported by Savéant[2] for the electron hopping process, if $C_A + C_B$ is assumed to be the total site concentration $C_T$ i.e., in the absence of vacant sites.

Similarly for the redox species A moving through vacancy, the forward and reverse fluxes of A between the two sites 1 and 2′ (where the 2′ site is vacant) separated by a distance $\Delta\gamma$ can be represented as

$$(\vec{J}_A)_{phys} = {}^1\!/_2 \Delta\gamma\vartheta'_{AV}(1 + \xi_{phys})C_{A,1} \qquad (B\text{-}6a)$$

$$(\overset{\leftarrow}{J}_A)_{phys} = {}^1\!/_2 \Delta\gamma\vartheta'_{AV}(1 - \xi_{phys})C_{A,2'} \qquad (B\text{-}6b)$$

where $\vartheta'_{AV}$ denotes the rate constant for unimolecular displacement of the redox ion and $\xi$ is the dimensionless force represented as $\xi_{phys} = \pm(z_iF\Delta\gamma/2RT)(\partial\varphi/\partial x)$. The net flux of A due to physical diffusion is given as

$$J^A_{phys} = (\vec{J}_A)_{phys} - (\overset{\leftarrow}{J}_A)_{phys} \qquad (B\text{-}7)$$

$$J^A_{phys} = {}^1\!/_2 \Delta\gamma\vartheta'_{AV}[(1 + \xi_{phys})C_{A,1} - (1 - \xi_{phys})C_{A,2'}] \qquad (B\text{-}8)$$

This leads to the flux for physical displacement, viz.

$$J^A_{phys} = {}^1\!/_2 \Delta\gamma^2\vartheta'_{AV}\left[-\frac{\partial C_A}{\partial x} - \frac{C_A z_A F}{RT}\frac{\partial\varphi}{\partial x}\right] \qquad (B\text{-}9)$$

Interestingly, the Nernst−Planck equation is valid despite the introduction of another competitive process, viz., electron hopping, because the movement of A through vacancies is independent of the electron exchange between A and B. Since the range of physical diffusion is unique for each species, we use the mean squared displacement, $\Delta\gamma^2$ instead of $\gamma^2$. Equations B-5 and B-9 can be rewritten in terms of fractional concentrations as

$$J^A_{hop} = -D_{hop}C_T\left[\frac{\partial\chi_A}{\partial x} - \frac{\chi_A\chi_B}{\chi}\frac{nF}{RT}\frac{\partial\varphi}{\partial x}\right] \qquad (B\text{-}10)$$

$$J^A_{phys} = -D^A_{phys}C_T\left[\frac{\partial\chi_A}{\partial x} + \frac{z_A\chi_A F}{RT}\frac{\partial\varphi}{\partial x}\right] \qquad (B\text{-}11)$$

where $D_{hop} = \vartheta_{AB}\delta^2 C°/2$ and $D^A_{phys} = \vartheta'_{AV}\Delta\gamma^2/2$. The flux of A through the polymer film can take place both by electron

hopping and physical diffusion. The contribution of each mode of transport toward the total flux of A depends on the availability of vacancies for physical diffusion and occupied sites for electron hopping. Hence the total flux is represented as a weighted sum of these two fluxes:

$$J_{Total}^{A} = \chi J_{hop}^{A} + f(1 - \chi)J_{phys}^{A} \tag{B-12}$$

Here $\chi$ and $1 - \chi$ are the fractions of occupied and vacant sites respectively, and $f$ is the correlation factor in one dimension (cf. section, 2.1). Hence, $J_{Total}^{A}$ becomes[41]

$$J_{Total}^{A} = -[D_{hop}\chi + fD_{phys}^{A}(1 - \chi)]C_{T}\frac{\partial \chi_{A}}{\partial x} +$$
$$\frac{FC_{T}}{RT}[D_{hop}\chi_{A}\chi_{B}n - fD_{phys}^{A}\chi_{A}z_{A}(1 - \chi)]\frac{\partial \varphi}{\partial x} \tag{B-13}$$

Since the number of electrons $n$ equals $z_{B} - z_{A}$, we obtain

$$J_{Total}^{A} =$$
$$-D_{ap}C_{T}\left\{\frac{\partial \chi_{A}}{\partial x} + \frac{F}{RT}\left[\chi_{A}z_{A} - \frac{D_{hop}}{D_{ap}}\chi_{A}(\chi_{A}z_{A} + \chi_{B}z_{B})\right]\frac{\partial \varphi}{\partial x}\right\}$$
$$\tag{B-14}$$

where

$$D_{ap} = D_{hop}\chi + fD_{phys}(1 - \chi) \tag{B-15}$$

Equation B-14 is identical with eq 3 of the text. The flux of B can be represented in a similar manner. We have assumed $D_{phys}^{A} = D_{phys}^{B}$ which implies that A and B are diffusing at the same rate in the case of physical diffusion. Equation B-14 represents the flux equation for competitive charge transport systems with both bounded and freely diffusing redox sites, albeit with different ansatz for $D_{phys}$ and calculation of vacant sites.

## References and Notes

(1) (a) Murray, R. W. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1984; Vol. 13. (b) Inzelt, G. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1994; Vol.18.

(2) Savéant, J. M. *J. Electroanal. Chem.* **1986**, *201*, 211.

(3) Buck, R. P. *J. Phys. Chem.* **1988**, *92*, 4196.

(4) Denny, R. A.; Sangaranarayanan, M. V. *J. Phys. Chem. B.* **1998**, *102*, 2131.

(5) (a) Chidsey, C. E. D.; Murray, R. W. *J. Phys. Chem.* **1986**, *90*, 3850. (b) Vorotyntsev, M. A.; Daikhin, L. I.; Levi, M. D. *J. Electroanal. Chem.* **1994**, *364*, 37.

(6) Srinivasamohan, L.; Sangaranarayanan, M. V. *J. Electroanal. Chem.* **1992**, *323*, 375. (b) Blauch, D. N.; Savéant, J. M. *J. Phys. Chem.* **1993**, *97*, 6444.

(7) (a) Dahms, H. *J. Phys. Chem.* **1968**, *72*, 362. (b) Ruff, I.; Friedrich, V. J. *J. Phys. Chem.* **1971**, *75*, 3297. (c) Ruff, I.; Friedrich, V. J.; Demeter, K.; Csaillag, K. *J. Phys. Chem.* **1971**, *75*, 3303. (d) Ruff, I.; Botár, L. *J. Chem. Phys.* **1985**, *83*, 1292. (e) Botár, L.; Ruff, I. *Chem. Phys. Lett.* **1986**, *126*, 348.

(8) Blauch, D. N.; Savéant, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 3323.

(9) (a) Martin, C. R.; Dollard, K. A. *J. Electroanal. Chem.* **1983**, *159*, 127. (b) Doblhoffer, K.; Lange, R. *J. Electroanal. Chem.* **1987**, *229*, 239. (c) Anson, F. C.; Savéant, J. M.; Shigehara, K. *J. Am. Chem. Soc.* **1983**, *105*, 1096. (d) Rubinstein, I.; Bard, A. J. *J. Am. Chem. Soc.* **1981**, *103*, 5007.

(10) (a) Facci, J. S.; Murray, R. W. *J. Phys. Chem.* **1981**, *85*, 287 (b) Facci, J. S.; Schmehl, R. H.; Murray, R. W. *J. Am. Chem. Soc.* **1982**, *104*, 4959. (c) Kuo, K.; Murray, R. W. *J. Electroanal. Chem.* **1982**, *131*, 37.

(11) (a) Nakazato, K.; Kitahara, K. *Prog. Theor. Phys.* **1986**, 64, 2261. (b) Murch, G. E.; Thorn, R. *Philos. Mag. A* **1979**, *39*, 673. (c) Koiwa, M.; Ishioka, S. *J. Stat. Phys.* **1983**, *30*, 477.

(12) Terrill, R. H.; Shechan, P. E.; Long, V. C.; Washburn, S.; Murray, R. W. *J. Phys. Chem.* **1994**, *98*, 5127.

(13) We have assumed $k_{ex}$ to be $1 \times 10^{6}$ M$^{-1}$ s$^{-1}$, $\delta$ to be 6 Å, and $f$ as 0.3 in the calculation of apparent diffusion coefficient and ignored the variation of $f$ with the concentration of vacancies.

(14) (a) Sharp, M.; Lindholm, B.; Lind, E. *J. Electroanal. Chem.* **1989**, *274*, 35. (b) Abraham John, S.; Ramaraj, R. *Proc. Indian Acad. Sci. (Chem. Sci.)* **1998**, *110*, 115.

(15) Bonhôte, P.; Gogniat, E.; Tingry, S.; Barbé, C.; Vlachopoulos, N.; Lenzmann, F.; Comte, P.; Grätzel, M. *J. Phys. Chem. B* **1998**, *102*, 1498.

(16) Kumins, C.A.; Kwei, T.K. In *Diffusion in Polymers*; Crank, J., Dark, G. S., Eds.; Academic Press: New York, 1968; p 107.

(17) Lyons, M. E. G. In *Annual Reports on the Progress of Chemistry, Section C, Physical Chemistry*; The Royal Society of Chemistry: Cambridge, UK, 1990; Vol. 87, p 158.

(18) (a) Tsou, Y.; Anson, F. C. *J. Phys. Chem.* **1985**, *89*, 3818. (b) Whiteley, L. D.; Martin, C.R. *J. Phys. Chem.* **1989**, *93*, 4650.

(19) (a) White, H. S.; Leddy, J.; Bard, A.J. *J. Am. Chem. Soc.* **1982**, *104*, 4811. (b) Martin, C. R.; Rubinstein, I.; Bard, A. J. *J. Am. Chem. Soc.* **1982**, *104*, 4817. (c) Rubinstein, I. *J. Electroanal. Chem.* **1985**, *188*, 227.

(20) (a) Gurland, J. *Trans. Met. Soc.* AIME **1966**, *236*, 642. (b) Malliaris, A.; Turner, D. T. *J. Appl. Phys.* **1971**, *42*, 614. (c) Last, B. J.; Thouless, D. J. *Phys. Rev. Lett.*, **1971**, *27*, 1719.

(21) Pourcelly, G.; Oikonomou, A.; Gavach, C.; Hurwitz, H. D. *J. Electroanal. Chem.* **1990**, *287*, 43.

(22) (a) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155. (b) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679.

(23) (a) Hupp, J. T.; Weaver, M. J. *J. Electroanal. Chem.* **1983**, *152*, 1. (b) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441.

(24) McManis, G. E.; Nielson, R. M.; Gochev, A.; Weaver, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 5533.

(25) Mathias, M. F.; Haas, O. *J. Phys. Chem.* **1993**, *97*, 9217.

(26) Dalton, E. F.; Surridge, N. A.; Jernigan, J. C.; Wilbourn, K. O.; Facci, J. S.; Murray, R. W. *Chem. Phys.* **1990**, *141*, 143 and references therein.

(27) Jernigan, J. C.; Murray, R. W. *J. Phys. Chem.* **1987**, *91*, 2030.

(28) (a) Mathias, M. F.; Haas. O. *J. Phys. Chem.* **1992**, *96*, 3174. (b) Láng, G.; Inzelt, G. *Electrochim. Acta* **1999**, *44*, 2037.

(29) Yang, H.; Tianhong, L.; Xue, K.; Sun, S.; Lu, G.; Chen, S. *J. Electrochem. Soc.* **1997**, *144*, 2302.

(30) Elmgren, M.; Lindquist, S.; Henriksson, G. *J. Electroanal. Chem.* **1992**, *341*, 257.

(31) Giovani, W.; Deronzier, A. *J. Electroanal. Chem.* **1992**, *337*, 285.

(32) Denny, R. A.; Sangaranarayanan, M. V. *J. Phys. Chem. B.* **1998**, *102*, 2138.

(33) Thus we obtain a nonlinear variation of $D_{ap}(E_{eq})$ with potential at $E°'$ only when $D_{phys} < 1 \times 10^{-15}$ cm$^{-2}$ s$^{-1}$. When $D_{phys} > 1 \times 10^{-15}$ cm$^2$ s$^{-1}$ the magnitude of $D_{ap}(E_{eq})$ at potentials away from the formal potential are larger due to physical diffusion as compared to that observed as a result of electron hopping at the formal potential. Thus we obtain essentially $D_{ap}(E_{eq})$ invariant with potential.

(34) Newman, J. S. In *Electrochemical Systems*; Prentice Hall: Englewood Cliffs NJ, 1973.

(35) Denny, R. A.; Sangaranarayanan, M. V. *J. Phys. A: Math. Gen.* **1998**, *31*, 7671.

(36) (a) He, P.; Chen, X. *J. Electroanal. Chem.* **1988**, *256*, 353. (b) Fritsch-Faules, I.; Faulkner, L. R. *J. Electroanal. Chem.* **1989**, *263*, 237.

(37) Buttry, D. A.; Anson, F. C. *J. Am. Chem. Soc.* **1983**, *105*, 685.

(38) Denny, R. A.; Sangaranarayanan, M. V. *J. Phys. Chem. B.* **1998**, *102*, 8670.

(39) We have assumed the following values in our calculations: area of the film = 0.1 cm$^2$; thickness = 2 $\mu$m; diameter of the ion $(2R)$ = 6 Å (we have employed equal values for $\delta$ and $2R$ as an approximation. Note that $\delta$ itself is a function of concentration of occupied sites;[10b] density of the film = 2 g cm$^{-3}$; equivalent weight of the polymer = 970 g equiv$^{-1}$ which lead to the polymer film concentration of 2.06 M from eq A-4. Thus, we obtain the concentration of vacancy to be 5.6 M using eq A-5.

(40) The volume of the redox polymeric film may change as the redox reaction proceeds due to the intake or the expulsion of the counterions depending upon the nature of the electrochemical reaction.

(41) (a) A similar analysis is available for the transport of point defects in passive films[41b] albeit without the blocking factor $\chi$. (b) Zhang, L.; Macdonald, D. D. *Electrochim. Acta* **1988**, *43*, 679.

(42) Savéant, J. M. *J. Phys. Chem.* **1988**, *92*, 4526.