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Mathematical Modelling of Transport through Conducting Polymer Films.
I. Theoretical Consideration

by

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Abstract

A mathematical model is presented which describes the electrochemical behavior of some polymer electrode systems. Current flow is described in terms of the diffusion and migration of ions in the polymer matrix, which leads to an overpotential gradient in the film. The model is used to describe the transient current response at a conducting polymer-modified electrode.

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MATHEMATICAL MODELLING OF TRANSPORT

THROUGH CONDUCTIVE POLYMER FILMS

I. THEORETICAL CONSIDERATIONS

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Introduction

Conductive polymers such as poly(acetylene) (PA), poly(pyrrole) (PP), and poly(paraphenylene) (PPP) have received much attention recently due to their potential applications and also because of interest in their fundamental properties. Much effort has been placed into describing the mechanism of charge transport through polymer films. Descriptions of the basic transport properties of conducting polymers focussed initially on microscopic mathematical transport models where "electron hopping" [1-12] between adjacent oxidized and reduced sites in redox polymer films was suggested to be the mechanism of charge transfer. Later it became apparent that a consideration of concurrent molecular diffusion of ions [13-16] within the polymer matrix was necessary to account for observed polymer film behavior. The most popular treatment has involved coupling electron self-exchange reactions within the matrix with counterion diffusion in the polymer film [14, 17-26]. This has led to a consideration of the measured diffusion coefficient (D_{exp}) as being comprised of contributions due to ion diffusion (D_o) and "electron diffusion" (D_{et}). Treated in this manner, different polymer materials will have different values of electron transfer diffusion coefficient and will thereby have different conductivities. To date the contribution of the charge transfer (electron) diffusion coefficient to overall film transport behavior has been regarded as fundamental in describing the transport characteristics of most conductive polymers [27-30]. In some cases the contribution of "electron hopping" to the overall transport in various modified electrodes has been determined to be negligible [31, 32], and ion diffusion coefficients within polymer films have been measured experimentally.

Most workers have neglected the effects of migration on the measured overall current. Descriptions of charge transport phenomena have been ascribed primarily

to diffusional effects, and have excluded other mass transport contributions to the measured flux. Yap and Durst [33, 34] were the first to theoretically consider the effects of migration. Lange and Doblhofer [35, 36] have experimentally verified migrational contributions in some conducting polymers using a rotating ring-disc electrode, while Elliot [31] and Osteryoung [32] have observed migrational effects in some polymer electrodes voltammetrically.

In this paper a more detailed transport model will be proposed which takes into account the migrational and diffusional contributions to the overall measured flux through the film. Yap and Durst [33, 34] have proposed macroscopic models which include migrational effects, based on the assumption of a constant electric field in the polymer film. In the model presented herein a varied potential gradient exists across the polymer; this must be determined by the local concentrations of all ionic species in the solution within the film, and by the electrical conductivity of the film. The model is based upon an approach used initially in describing the behavior of porous battery materials [37-42]. In this modelling scheme the temporal behavior of the expected current response due to an applied potential step is predicted theoretically and computed numerically via a Runge-Kutta method.

Experimental

Numerical digital simulations describing the electrochemical behavior of model polymer films were carried out on an IBM PC/AT. Two computer programs (available from the authors) utilizing a fourth-order Runge-Kutta algorithm combined with a shooting method and an Adams predictor-corrector were implemented (for similar algorithms describing the solution of coupled differential equations, see the appropriate sections in refs. [43 and 44]). In the first

program, the initial conditions of the system are set up, and the local parameters in the film determined (overpotential, current, conversion as a function of position in the film) for the first time increment by a shooting algorithm. These values are then used as starting values in the second program which evaluates the local overpotential-, current-, and conversion-distance profiles in subsequent time increments. Simulated chronoamperograms are constructed by integrating the resultant local current-distance profiles and examining the temporal behavior of the total (simulated) current. Cottrell and chronocoulometric plots are subsequently constructed.

The Theoretical Model

The Basis of the Model

It is assumed initially that the charge (and discharge) of the model polymer film is controlled purely by diffusion and migration of the supporting electrolyte within the polymer matrix. Any electrochemical process that occurs in the heterogeneous polymer medium will be controlled by the local electrochemical potential, which in turn will have a time dependency determined by the rate of mass transport of the ions in the medium. The Galvani potential of electrons in the polymer phase, ϕ_p, is constant, and movement of charge is fast compared with movement of charge in the solution phase. Sites in the polymer are converted at random from neutral to oxidized form (essentially a Langmuir model), with the process being kinetically controlled and driven by the difference in Galvani potentials between the polymer and solution phases.

We shall begin with the expression for the local rate of reaction [45, 46]:

$$\text{Rate} = k_f' C(o) \exp^{-}\left[\frac{\alpha(\phi_p - \phi_s)F}{RT}\right] -$$

$$k_b' C(+) \exp\left[\frac{(1-\alpha)(\phi_p - \phi_s)F}{RT}\right] \qquad (1)$$

where k_f' is the heterogeneous rate constant for the forward reaction, k_b' is that for the reverse reaction, α is the transfer coefficient, ϕ_s is the Galvani potential of electrons in the solution phase, F is the Faraday constant, R is the gas constant, T is the absolute temperature, and $C(o)$, $C(+)$ represent the concentrations of neutral and oxidized forms of polymer within the film matrix, respectively. The conversion of neutral into oxidized form is expressed as

$$\chi = C(+)/C^o(o) \qquad (2)$$

where $C^o(o)$ is the concentration of neutral polymer in the completely unoxidized film. Then

$$(1-\chi) = C(o)/C^o(o) \quad . \qquad (3)$$

Inclusion of $C^o(o)$ in the definition of the rate constants yields

$$\text{Rate} = k_f \chi \exp^{-}\left[\frac{\alpha(\phi_p - \phi_s)F}{RT}\right] - k_b(1-\chi)\exp\left[\frac{(1-\alpha)(\phi_p - \phi_s)F}{RT}\right] \quad . \qquad (4)$$

Notice that $k_f = k_f' C^o(o)$ and $k_b = k_b' C^o(o)$.

We assume the value of $\chi = 0.5$ as the definition of a standard state where the difference in Galvani potentials is $(\phi_p - \phi_s)^o$. We have

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$$\phi_p - \phi_s = (\phi_p - \phi_s)^o + \eta \qquad (5)$$

where the overpotential $\eta = -\Delta\phi_s$ and $\Delta\phi_s$ is the shift in the solution potential from the standard value. Then

$$\text{Rate} = k_f \chi \exp\left[\frac{\alpha(\phi_p-\phi_s)^o F}{RT}\right]\exp\left[\frac{\alpha\eta F}{RT}\right] -$$

$$k_b(1-\chi)\exp\left[\frac{(1-\alpha)(\phi_p-\phi_s)^o F}{RT}\right]\exp\left[\frac{(1-\alpha)\eta F}{RT}\right] . \qquad (6)$$

For equilibrium charging at $\alpha = 0.5$ and $\eta = 0$ the overall reaction rate equals zero, so

$$k_f \exp^-\left[\frac{\alpha(\phi_p-\phi_s)^o F}{RT}\right] = k_b \exp\left[\frac{(1-\alpha)(\phi_p-\phi_s)^o F}{RT}\right] = k^o \qquad (7)$$

and

$$\text{Rate} = k^o \exp^-\left[\frac{\alpha\eta F}{RT}\right]\{\chi - (1-\chi)\exp\left[\frac{\eta F}{RT}\right]\} \qquad (8)$$

per unit area.

The cation flux of the simple univalent electrolyte is

$$N_+ = -D_+\frac{\partial c_+}{\partial x} - c_+ u_+\frac{\partial\phi_s}{\partial x} \qquad (9)$$

where D_+ is the diffusion coefficient of the cation and c_+ and u_+ are its concentration and mobility, respectively; x is the distance coordinate in the film. A similar expression can be written to describe the flux of anions:

$$N_- = -D_- \frac{\partial c_-}{\partial x} + c_- u_- \frac{\partial \phi_s}{\partial x} \quad . \tag{10}$$

Assuming that electroneutrality holds in the solution phase (i.e., $c_+ = c_- = c$), we have for the local current density

$$I = F(N_+ - N_-) = -F(D_+ - D_-)\frac{\partial c}{\partial x} - Fc(u_+ + u_-)\frac{\partial \phi_s}{\partial x} \quad , \tag{11}$$

i.e.,

$$\frac{\partial \phi_s}{\partial x} = - \frac{I}{Fc(u_+ + u_-)} - \frac{(D_+ - D_-)}{c(u_+ + u_-)}\frac{\partial c}{\partial x} \quad . \tag{12}$$

Substituting (12) into (9),

$$N_+ = -D_+ \frac{\partial c}{\partial x} + \frac{u_+ I}{F(u_+ + u_-)} + \frac{u_+(D_+ - D_-)}{u_+ + u_-}\frac{\partial c}{\partial x} \tag{13a}$$

$$= \frac{t_+ I}{F} - D \frac{\partial c}{\partial x} \tag{13b}$$

where the transport number $t_+ = u_+/(u_++u_-)$ and the binary diffusion coefficient D $= 2D_+D_-/(D_++D_-)$.

Alternatively, N_+ can be expressed in terms of I and $\partial\phi_s/\partial x$. We may now take the divergence of (13) and, noting that

$$\frac{\partial I}{\partial x} = aF(Rate) = aFk^o exp^-[\frac{\alpha\eta F}{RT}]\{\chi-(1-\chi)exp[\frac{\eta F}{RT}]\} , \qquad (14)$$

where a is the specific area (equal to area/volume of the electroactive substrate), we arrive at

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} + \frac{(1-t_+)}{F}\frac{\partial I}{\partial x} . \qquad (15)$$

Or we may write

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} + (1-t_+)ak^o exp^-[\frac{\alpha\eta F}{RT}]\{\chi-(1-\chi)exp[\frac{\eta F}{RT}]\} . \qquad (16)$$

The numerical calculation is begun by assuming a quasi-stationary state [39]:

$$D\frac{\partial^2 c}{\partial x^2} + \frac{(1-t_+)}{F}\frac{\partial I}{\partial x} = c . \qquad (17)$$

As these equations always contain c, x, and η, it will be necessary to do a stepwise, iterative calculation [47].

In the quasi-stationary state (17) can be integrated once to

$$\frac{\partial c}{\partial x} = -\frac{(1-t_+)}{FD} I , \qquad (18)$$

while I is given by (14). The boundary conditions at the surface are $I = 0$, $\partial c/\partial x = 0$, $\partial \eta/\partial x = 0$, $x = 0$, where $x = 0$ is the surface of the polymer film adjacent to the electrode. The boundary conditions at the polymer/ solution junction $(x = \ell)$ are $c = c^\infty$, $\eta = \eta_{applied} = -(\phi_s)_{applied}$, where c^∞ is the bulk concentration and ℓ is the thickness of the film.

Having lumped together the effects of reaction and transport into one equation to give $\partial c/\partial t$ we must return to the basic flux equation (11) and write this

$$I = -F(D_+ - D_-)\frac{\partial c}{\partial x} + F(u_+ + u_-)c \frac{\partial \eta}{\partial x} . \qquad (19)$$

Diffusion coefficients and mobilities within polymer electrodes are often experimentally determinable [31,32]; if they are unknown, it may initially be assumed that they are given by the solution phase values. In addition, we start with the initial conditions $x = 0$, $c = \Delta c$, $0 < x < \ell$; $t = 0$, where Δc is a finite quantity and the initial electrolyte content of the polymer is assumed to be equal to the bulk concentration.

The scheme for the numerical calculation is as follows:

i. An initial overpotential value η_i is chosen, and the initial value of χ_i is calculated from

$$\chi_i - (1-\chi_i)\exp\left[\frac{\eta_i F}{RT}\right] - 0 \quad . \tag{20}$$

ii. We choose the working overpotential η_f, and initiate the calculation by substituting (18) into (1º) and carrying out a simultaneous integration of (14) and (19) to satisfy the boundary conditions at $x - 0$. Observe that if $I - 0$ and $\partial\eta/\partial x - 0$ at $x - 0$, then $\partial\phi/\partial x - 0$ automatically by virtue of (18) (or (19)). I is chosen at $x - \ell$ to ensure that we obtain the boundary value at the polymer film/ solution interface.

iii. Having derived $I - f_1(x)$ we derive $c - f_2(x)$ and $\chi - f_3(x)$ and use these fixed values for the next step of the calculation. In determining $\chi - f_3(x)$ it is assumed that $I - f_1(x)$ remains fixed over the time interval Δt. Also, in calculating $c - f_2(x)$ we must assume a value of c at $x - \ell$ which remains constant over the duration of the experiment.

iv. The calculation is then extended to the non-steady state. Having found in steps i.-iii.) an initial overpotential η_i which satisfies the boundary conditions at $x - \ell$, this value can then be introduced into a program which calculates the conversion-distance profiles at various times using a non-steady state approach. The local currents and local overpotentials at varying distances in the film are calculated iteratively, and temporal changes in these currents

distance and overpotential-distance profiles are computed using a fourth order Runge-Kutta numerical method coupled with a shooting method and Adams predictor-corrector [43, 44, 48].

Special Cases

Consider first the case where slow mass transfer occurs through the solution phase in the polymer matrix, and charge mobility in the polymer phase is very fast. Taking $D_+ = D_-$ and $\alpha = 0.5$, we have

$$I = F(u_+ + u_-)c \frac{\partial \eta}{\partial x} , \qquad (21)$$

i.e., the concentration gradient of electrolyte in the polymer film is eliminated. Differentiating (21) and combining with (14) we arrive at

$$\frac{d^2\eta}{dx^2} - \frac{k^o}{(u_+ + u_-)c} \exp^- \frac{\alpha \eta F}{RT}[\chi - (1-\chi)\exp \frac{\eta F}{RT}] = 0 . \qquad (22)$$

The solution of this differential equation follows the same form as the problem of porous battery electrodes which has been treated previously [47, 49]. A first step in obtaining a solution is to write

$$\frac{d^2\eta}{dx^2} = \frac{1}{2} \frac{d}{d\eta}(\frac{d\eta}{dx})^2 = \Gamma \exp^- \frac{\alpha \eta F}{RT}[\chi - (1-\chi)\exp \frac{\eta F}{RT}] , \qquad (23)$$

where $\Gamma = k^o/(u_+ + u_-)c$. Integrating, we have

$$\left(\frac{d\eta}{dx}\right)^2 = \frac{RT\chi\Gamma}{\alpha F}\exp^-\frac{\alpha\eta F}{RT} - \frac{RT(1-\chi)\Gamma}{(1-\alpha)F}\exp\frac{(1-\alpha)\eta F}{RT} + \text{constant} . \quad (24)$$

Note that at $x = 0$, $d\eta/dx = 0$, and $\eta = \eta_0$ where η_0 is determined via the previously described shooting method. Therefore

$$\text{constant} = \frac{RT\chi\Gamma}{\alpha F}\exp^-\frac{\alpha\eta_0 F}{RT} + \frac{RT(1-\chi)\Gamma}{(1-\alpha)F}\exp\frac{(1-\alpha)\eta_0 F}{RT} , \quad (25)$$

and

$$\frac{d\eta}{dx} = \left\{\frac{RT\chi\Gamma}{\alpha F}\left[\exp^-\frac{\alpha\eta_0 F}{RT} - \exp^-\frac{\alpha\eta F}{RT}\right] + \right.$$

$$\left. \frac{RT(1-\chi)\Gamma}{(1-\alpha)F}\left[\exp\frac{(1-\alpha)\eta_0 F}{RT} - \exp\frac{(1-\alpha)\eta F}{RT}\right]\right\}^{\frac{1}{2}} . \quad (26)$$

From (26),

$$x = \int_{\eta_0}^{\eta}\left\{\frac{RT\chi\Gamma}{\alpha F}\left[\exp^-\frac{\alpha\eta_0 F}{RT} - \exp^-\frac{\alpha\eta' F}{RT}\right] + \right.$$

$$\left. \frac{RT(1-\chi)\Gamma}{(1-\alpha)F}\left[\exp\frac{(1-\alpha)\eta_0 F}{RT} - \exp\frac{(1-\alpha)\eta' F}{RT}\right]\right\}^{-\frac{1}{2}} d\eta' \quad (27a)$$

$$= \int_{\eta_0}^{\eta}\left(ab - a\cdot\exp^-\frac{\alpha\eta' F}{RT} + ef - e\cdot\exp\frac{(1-\alpha)\eta' F}{RT}\right)^{-\frac{1}{2}} d\eta' \quad (27b)$$

where a, b, e, and f are evident from the equation.

The strategy of the numerical calculation is as follows. η_0 is chosen so is

to render $\eta = \eta_{applied}$ at $x = \ell$ (recall that $\eta_{applied}$ is given by the measured current at the polymer/solution interface for an equipotential polymer surface). By integrating (27) we determine $x = f(\eta)$ and hence $\eta = g(x)$. From this the change in x in steps of time can be calculated. The current is derived from (21) at $x = \ell$ and, adding the assumption $\alpha = 0.5$, we have

$$x = \int_{\eta_o}^{\eta} \left(\frac{2RT\chi\Gamma}{F}[\exp^- \frac{\eta_o F}{2RT} - \exp^- \frac{\eta' F}{2RT}] + \frac{2RT(1-\chi)\Gamma}{F}[\exp\frac{\eta_o F}{2RT} - \exp\frac{\eta' F}{2RT}]\right)^{-\frac{1}{2}} d\eta' . \qquad (28)$$

Now let us consider the case of low charge mobility in the polymer phase coupled with high mobility of charge in the solution phase, with the solution at an equipotential. Now ϕ_s = constant, so $\eta = \Delta\phi_p$, and the rate of reaction is still given by eq. (8). Where before it was possible to ignore charge flow in the polymer phase, in this case the charge flow in the solution phase may be ignored. The charge flux in the polymer phase is expressed as

$$N_+ = -D_+ \frac{\partial c_+}{\partial x} - u_+ c_+ \frac{\partial \phi_p}{\partial x} ; \qquad (29)$$

observe that u_+ is likely to be dependent on c_+. A probable functional relationship is electron transfer between occupied and unoccupied sites, expressed macroscopically as

$$u_+ c_+ = u_+'(1-\chi)c_o\chi \qquad (30)$$

where u_+' is the cation mobility in the unconverted form of the film, and c_o is the initial electrolyte concentration. Now

$$I = F(-D_+\frac{\partial c_+}{\partial x} - u_+'(1-x)xc_o\frac{\partial\eta}{\partial x}) .$$ (31)

Applying the Nernst-Einstein relation,

$$D_+ = \frac{RT}{F}u_+ ,$$ (32)

we have

$$I = -F(\frac{RT}{F}u_+\frac{\partial c_+}{\partial x} + u_+'(1-x)xc_o\frac{\partial\eta}{\partial x})$$ (33a)

$$= -Fu_+'(1-x)xc_o(\frac{RT}{Fx}\frac{\partial x}{\partial x} + \frac{\partial\eta}{\partial x}) ,$$ (33b)

which must be coupled with

$$\frac{\partial I}{\partial x} = Fk^o exp^-\frac{\alpha\eta F}{RT}[x-(1-x)exp\frac{\eta F}{RT}] .$$ (34)

The boundary conditions are $I = 0$, $\partial\eta/\partial x = 0$ at $x = \ell$; $\eta = \eta_f$ at $x = 0$, with the initial value of x being determined by η_i. The numerical calculation is carried out as before except that (18) cannot be substituted into (33); rather, $\partial x \partial x$ must be kept fixed for each step of the calculation.

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Consider the case where there is low charge mobility in the polymer as well as low mobility of anions in the film. Now (29) is combined with (10) and it is assumed that electroneutrality still holds, i.e., $c_+ = c_- = c$. Two fluxes (or currents I_+ and I_-) must now be considered:

$$\frac{I_+}{F} = N_+ = -D_+\frac{\partial c}{\partial x} - u_+ c\frac{\partial \phi_p}{\partial x} \qquad (35)$$

$$\frac{I_-}{F} = N_- = -D_-\frac{\partial c}{\partial x} + u_- c\frac{\partial \phi_s}{\partial x} \ , \qquad (36)$$

and the boundary conditions are $\partial N_+/\partial x = 0$ at $x = \ell$, and $FN_+ = I_T$ at $x = 0$ (where I_T is the measured current in the external circuit); $\partial N_-/\partial x = 0$ at $x = 0$, $FN_- = I_T$ at $x = \ell$. Observe that D_+ and u_+ may be markedly dependent upon c_+ (i.e., χ), whereas D_- and u_- will not vary appreciably with c. The anion flux can be expressed as

$$N_- = -D_- c_0\frac{\partial \chi}{\partial x} + u_- c_0\chi\frac{\partial \phi_s}{\partial x} \qquad (37)$$

whereas we must use (30) or $u_+ = u_+'$ (where u_+ is in this instance independent of concentration) to express u_+ and D_+. With (30),

$$N_+ = -u_+'(1-\chi)\chi c_0(\frac{RT}{F}\frac{1}{\chi}\frac{\partial \chi}{\partial x} + \frac{\partial \phi_p}{\partial x}) \ . \qquad (38)$$

The divergences of these fluxes will be equal since the accumulation of (+) form of the polymer (making no assumption as to the identity of the positive charge, be it in the form of polarons, bipolarons, or charged solitons.) is equal to the accumulation of anions, i.e.,

$$\frac{\partial N_+}{\partial x} = \frac{\partial N_-}{\partial x} = k^o \exp^- \frac{\alpha(\phi_p - \phi_s)F}{RT} [\chi - (1-\chi)\exp\frac{(\phi_p - \phi_s)F}{RT}] \quad . \quad (39)$$

We may write

$$\frac{N_-}{u_- c_o \chi} = -\frac{D_- c_o}{u_- c_o \chi}\frac{\partial \chi}{\partial x} + \frac{\partial \phi_s}{\partial x} \quad , \quad (40a)$$

$$= -\frac{RT}{F}\frac{1}{\chi}\frac{\partial \chi}{\partial x} + \frac{\partial \phi_s}{\partial x} \quad , \quad (40b)$$

$$\frac{N_+}{u_+'\chi(1-\chi)c_o} = -\frac{RT}{F\chi}\frac{\partial \chi}{\partial x} - \frac{\partial \phi_p}{\partial x} \quad . \quad (41)$$

Adding (40) and (41),

$$\frac{1}{c_o \chi}(\frac{N_-}{u_-} + \frac{N_+}{u_+'(1-\chi)}) = -\frac{2RT}{F\chi}\frac{\partial \chi}{\partial x} \cdot \frac{\partial \eta}{\partial x} \quad (42)$$

or

$$\frac{N_-}{u_-} + \frac{N_+}{u_+'(1-\chi)} = -\frac{2RTc_o}{F}\frac{\partial \chi}{\partial x} \cdot c_o \chi \frac{\partial \eta}{\partial x} \quad , \quad (43)$$

which can be combined with (39) in the usual form:

$$\frac{\partial I_+}{\partial x} - \frac{\partial I_-}{\partial x} = Fk^o exp^- \frac{\alpha \eta F}{RT} [\chi - (1-\chi) exp \frac{\eta F}{RT}] \quad . \quad (44)$$

In order to solve (43) with (44) note that in addition

$$I_+ + I_- = I_T \qquad (45)$$

or

$$FN_+ + FN_- = I_T \quad , \qquad (46)$$

so

$$\frac{I_-}{u_-} + \frac{(I_T - I_-)}{u_+'(1-\chi)} = -2RTc_0 \frac{\partial \chi}{\partial x} - Fc_0 \chi \frac{\partial \eta}{\partial x} \quad . \qquad (47)$$

In carrying out the iterative calculation we must "shoot" to the final value of I_T which must be adjusted within the calculation at each step.

Consider the case where local equilibrium is assumed, i.e.,

$$\frac{\chi}{1-\chi} = exp \frac{\eta F}{RT} \quad . \qquad (48)$$

This gives

$$\frac{1}{(1-\chi)^2} \frac{d\chi}{dx} = \frac{F}{RT} exp \frac{\eta F}{RT} \frac{d\eta}{dx} \quad , \qquad (49)$$

or

$$\frac{d\eta}{dx} = \frac{RT}{F} \frac{1}{\exp(\eta F/RT)} \frac{1}{(1-\chi)^2} \frac{d\eta}{dx} \qquad (50a)$$

$$= \frac{RT}{F} \frac{1}{\chi(1-\chi)} \frac{d\chi}{dx} \quad . \qquad (50b)$$

Substituting into (47),

$$\frac{I_-}{u_-} + \frac{(I_T - I_-)}{u_+'(1-\chi)} = -2RTc_0\frac{\partial\chi}{\partial x} - \frac{RTc_0}{(1-\chi)^2}\frac{\partial\chi}{\partial x} \quad . \qquad (51)$$

We now numerically integrate, assuming as before that $\chi = f_1(x)$ is fixed within a given time step, and evaluate $I_- = f_2(x)$. This distribution is then used to determine the next set of values of $\chi = f_1(x)$.

Dimensionless Variables

In order to solve the preceding problems it is convenient to cast expressions in terms of dimensionless variables. Recall that

$$\frac{\partial I}{\partial x} = aF(Rate) = aFk^o\exp^-\frac{\alpha\eta F}{RT}[\chi - (1-\chi)\exp\frac{\eta F}{RT}] \quad , \qquad (14)$$

which must be solved with

$$I = -F(D_+ - D_-)\frac{\partial c}{\partial x} + F(u_+ + u_-)c\frac{\partial\eta}{\partial x} \quad . \qquad (19)$$

Taking into account that

$$\frac{\partial c}{\partial x} = -\frac{(1-t_+)}{FD}I \quad , \tag{18}$$

we have the following dimensionless variables:

$$f = \frac{\eta F}{RT} \quad , \tag{52}$$

$$i = \frac{I}{aFk^o} \quad , \tag{53}$$

$$y = \frac{x}{\ell} \quad , \tag{54}$$

$$C = \frac{c}{C(o)} \quad . \tag{55}$$

$$t = \frac{akTt}{C_{ppp(o)}} \tag{56}$$

Then (14) becomes

$$\frac{\partial i}{\partial y} = \exp^-(\alpha f[\chi-(1-\chi)\exp(f)]) \quad . \tag{57}$$

For the simulation we have the following parameters:

$$\ell$$

$$\beta = \frac{}{aFk^o} \quad , \tag{58}$$

$$\gamma = \frac{D_+ C(o)}{ak^o \ell} \quad , \tag{59}$$

(note that k^o depends on $C(o)$, i.e., γ is independent of $C(o)$), and

$$\lambda = \frac{D_-}{D_+} \quad . \tag{60}$$

Observe that β affects only the current amplitude, since

$$\int_o^\ell I \, dx = \beta \int_o^\ell i \, dy \quad . \tag{61}$$

γ and λ affect the shape of the modeled current transient via the relative rates of diffusion and migration, along with the volume rate of reaction. Eq. (19) becomes

$$i = -\gamma(1-\lambda)\frac{\partial C}{\partial y} + \gamma(1+\lambda)C\frac{\partial f}{\partial y} \quad , \tag{62}$$

while eq. (18) becomes

$$\frac{\partial C}{\partial y} = -\frac{i}{2\gamma} \quad . \tag{63}$$

The boundary conditions become $i = 0$, $\partial C/\partial y = 0$, $\partial f/\partial y = 0$ at $y = 0$; $C = C^{\infty}$, $f = f_{applied}$ at $y = 1$.

Changes in concentration and conversion from one step of the calculation to the next are estimated from

$$\Delta c = \frac{1}{F} \frac{\partial I}{\partial x} \Delta t \qquad (64)$$

where Δt is the time interval. This gives

$$\Delta \chi = \frac{ak^o}{C(o)} \frac{\partial i}{\partial y} \Delta t \quad , \qquad (65)$$

or

$$\Delta \chi = \frac{\partial i}{\partial y} \Delta \tau \qquad (66)$$

where $\Delta \tau = ak^o \Delta t/C(o)$. Substituting (63) into (62),

$$i(\frac{1+\lambda}{2}) = \gamma(1+\lambda)C \frac{\partial f}{\partial y} \quad , \qquad (67)$$

or

$$i = 2\gamma C \frac{\partial f}{\partial y} \quad . \qquad (68)$$

Thus the shape of the expected current transient is a function only of λ (and α).

Our task is to solve the simultaneous equations (68) and (57). Starting with $C =$ constant$_1$ and $\chi =$ constant$_2$, we iterate to obtain $i = f_1(y)$, deriving $C = f_2(y)$ and $\chi = f_3(y)$. To obtain the new value of χ we use (66), and the new concentration at each step is determined from

$$C = \text{constant}_1 - \int_0^y \frac{i}{2\gamma} \, dy \quad . \tag{69}$$

Let us apply a perturbation, taking a simple case where $f_0 = 0$, $\chi_0 = 0.5$, and $C = C_0$. We apply a perturbation $f = \Delta f$, where Δf is a small quantity. Then $C = C_0 + \Delta C$ and $\chi = \chi_0 + \Delta \chi$, where ΔC and $\Delta \chi$ are functions of y. Since Δf is small, then so is $\partial \Delta f / \partial y$. Therefore

$$i = 2\gamma(C_0 + \Delta C)\frac{\partial \Delta f}{\partial y} \simeq 2\gamma C_0 \frac{\partial \Delta f}{\partial y} \quad , \tag{70}$$

and

$$\frac{\partial i}{\partial y} = -\exp{-\alpha\Delta f}[(\chi_0 + \Delta\chi) - (1 - (\chi_0 + \Delta\chi)\exp\Delta f)]$$

$$\simeq -(1 - \alpha\Delta f)[(\chi_0 + \Delta\chi) - (1 - \chi_0 - \Delta\chi)(1 + \Delta f)]$$

$$= -(1 - \alpha\Delta f)[2\Delta\chi - 0.5\Delta f]$$

$$\simeq -2\Delta\chi + 0.5\Delta f \quad . \tag{71}$$

This can be used as an example to examine the Runge-Kutta numerical method. In the first iterative cycle $\Delta\chi = 0$, so

$$\frac{\partial i}{\partial y} = 0.5 \Delta f \quad . \qquad (72)$$

Differentiating

$$\frac{\partial \Delta f}{\partial y} = \frac{i}{2 \gamma C_o} \qquad (73)$$

yields

$$\frac{\partial^2 \Delta f}{\partial y^2} = \frac{1}{2 \gamma C_o} \frac{\partial i}{\partial y} = \frac{0.5 \Delta f}{2 \gamma C_o} \quad , \qquad (74)$$

or

$$\Delta f = A exp(\frac{0.5}{2 \gamma C_o})y + B exp^{-}(\frac{0.5}{2 \gamma C_o})y \quad . \qquad (75)$$

At $y = 0$, $\partial \Delta f / \partial y = 0$, or $\{(A \times 0.5)/(2 \gamma C_o) - (B \times 0.5)/(2 \gamma C_o)\} = 0$, i.e., $A = B$. At $y = 1$, $\Delta f = \Delta f_{y=1}$, so

$$\Delta f_{y=1} = A \{ exp(4 \gamma C_o)^{-1} + exp^{-}(4 \gamma C_o)^{-1} \} \quad . \qquad (76)$$

Therefore

$$A = \frac{2 \Delta f_{y=1}}{cosh[1/(4 \gamma C_o)]} \quad . \qquad (77)$$

Thus

$$\Delta f = \Delta f_{y=1} \frac{\cosh[1/(4\gamma C_o)]y}{\cosh[1/(4\gamma C_o)]} \qquad (78a)$$

$$\simeq \Delta f_{y=1} \frac{1+[1/(4\gamma C_o)]^2 y^2}{1+[1/(4\gamma C_o)]^2} \ . \qquad (78b)$$

C is regarded as a constant on the next cycle (cf. (73)).

Results and Discussion

Figures 1-3(a-c) show the simulated current-, conversion-, and overpotential-distance profiles for model polymer films of thickness ℓ as a function of varied γ (with $\alpha = 0.5$ in all cases). Figures 1-3(c-e) show the resultant simulated profiles as the variable C is varied. It is observed that as γ is increased, the initial local current increases with y, the conversion rate increases, and the overpotential gradient through the polymer layer decreases. Similar trends are observed for increases in the variable C.

In order to examine the simulated current-time transients expected during film charging, the local current at each point in time is integrated (via digital computer). This "measured" current (dimensionless) is then plotted as a function of dimensionless time τ. Figure 4 shows the simulated current-time profiles as a function of varied γ and C. It should be noted that contributions due to background charging current and capacitive current have not been included in these plots. Departure from Cottrell-like behavior (i.e., pure diffusion in a semi-infinite medium, which would predict $i \propto t^{-\frac{1}{2}}$) is due purely to the contribution of migrational effects coupled with slow diffusion processes within the polymer matrix of finite thickness.

The effects of migration [33] are seen more clearly in the simulated i vs. $t^{-\frac{1}{2}}$ plots (Figure 5) and in the theoretically predicted chronocoulometry (Figure 6), where there is observed significant departure from diffusion in a semi-infinite medium [45, 46]. The current vs. $t^{-\frac{1}{2}}$ plots deviate considerably from linearity, and charge is not proportional to $\sqrt{t}$.

These simulated chronoamperometric results differ from the simulations of Yap and Durst [33, 34], where it was assumed in their calculations that a constant electric field existed across the width of the polymer layer. In the above simulations, the existence of a varying potential gradient across the width of the film is included in the model, thereby accounting for the resulting differences from the simulations of Yap and Durst [33].

Conclusion

In this paper a macroscopic mathematical model has been proposed which describes the mass transport processes through conductive polymer-modified electrodes. The contributions of diffusion and migration have been included in the model; current-distance, conversion-distance, and overpotential-distance profiles as well as the overall simulated current-time transients have been derived as a function of the system parameters.[1] The proposed model will be the basis of other applications to polymer electrode systems.

Observations of deviations from diffusion-limited behavior are common in conductive polymer systems [31-36, 50-53], and models which describe charge transport in terms of diffusion processes alone are not sufficient for explaining

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[1]A recent paper dealing with the transient response of polymer coated electrodes under conditions of diffusion and migration of the redox ions has been published since we completed this manuscript. These authors have used an implicit finite difference technique. (Rainer Lange and Karl Doblhofer J. Electroanal. Chem. 237 (1987) 13).

transport in many conducting polymers. Hence, inclusion of migrational and other contributions into a transport model [54, 55] is often necessary in order to develop a more realistic view of transport and kinetic processes in polymer electrode systems.

Acknowledgment

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GLOSSARY OF SYMBOLS

a	Specific area, cm^{-1} (area/volume)
α	Transfer coefficient
β	Dimensionless parameter (ℓ/aFk°)
c	Electrolyte concentration, mols cm^{-3}
c_o	Initial electrolyte concentration, mols cm^{-3}
c_+	Electrolyte cation concentration, mols cm^{-3}
c_-	Electrolyte anion concentration, mols cm^{-3}
c^{∞}	Bulk electrolyte concentration, mols cm^{-3}
C	Dimensionless concentration, mols cm^{-3}
$C(o)$	Concentration of neutral polymer, mols cm^{-3}
$C(+)$	Concentration of oxidized polymer, mols cm^{-3}
$C^{\circ}(o)$	Initial concentration of neutral polymer, mols cm^{-3}
χ	Conversion of polymer ($C(+)/C^{\circ}(o)$)
χ_i	Initial conversion of polymer
χ_o	Initial conversion value
D	Binary diffusion coefficient, $cm^2 s^{-1}$
D_+	Electrolyte cation diffusion coefficient, $cm^2 s^{-1}$
D_-	Electrolyte anion diffusion coefficient, $cm^2 s^{-1}$
Δc	Change in electrolyte concentration, mols cm^{-3}
ΔC	Change in dimensionless concentration
$\Delta \chi$	Change in conversion
Δf	Change in dimensionless overpotential
$\Delta \phi_p$	Shift in Galvani potential of polymer phase, V
$\Delta \phi_s$	Shift in Galvani potential of solution phase, V
Δt	Time interval, s
$\Delta \tau$	Dimensionless time interval ($ak^{\circ}\Delta t/C(o)$)
η	Overpotential, V
η_f	Final overpotential at x=0, V
η_i	Initial overpotential, V
η_o	Overpotential at x=0, V
f	Dimensionless overpotential ($\eta F/RT$)
f_i	Initial dimensionless overpotential
F	Faraday constant, 96,484.6 C eq^{-1}
γ	Diffuso-kinetic dimensionless parameter ($D_+C(o)/a\ell k^{\circ}$)
Γ	Dimensionless parameter $(k^{\circ}/(u_++u_-)c)$
i	Dimensionless current ($I/aF\ell$)
I	Local current density, A cm^{-2}
I_+	Current density due to cation flux, A cm^2
I_-	Current density due to anion flux, A cm^{-2}
I_t	Total current density, A cm^{-2}
k_b	Concentration dependent rate constant reverse rcx, mol cm^2-s^{-1} ($k_b'C^{\circ}(o)$)
k_f	Concentration dependent rate constant forward rcx, mol cm^2-s^{-1} ($k_f'C^{\circ}(o)$)
k°	Standard heterogeneous rate constant, cm s^{-1}
k_b	Rate constant for reverse reaction, cm s^{-1}
k_f	Rate constant for forward reaction, cm s^{-1}
ℓ	Thickness of polymer layer, cm
λ	Dimensionless parameter (D_+/D_-)
N_+	Cation flux, $cm^2 s^{-1}$
N_-	Anion flux, $cm^2 s^{-1}$
ϕ_s	Galvani potential of solution phase, V

ϕ_p Galvani potential of polymer phase, V

R   Molar gas constant, 8.3144 J mol^{-1}-K^{-1}

t   Time, s

t_+ Cation transport number $(u_+/(u_++u_-))$

t_- Anion transport number $(u_-/(u_++u_-))$

T   Temperature, K

r Dimensionless time $(ak^\circ t/C(o))$

u_+ Electrolyte cation mobility, cm/s

u_- Electrolyte anion mobility, cm/s

x   Distance from electrode, cm

y   Dimensionless distance parameter (x/ℓ)

Figure Legends

Figure 1. Current vs. distance profiles for varied γ and C; α=0.5. (a) γ=1.0,C=0.5; (b) γ=10, C=0.5; (c) γ=100, C=0.5; (d) γ=100, C=0.3; (e) γ=100,C=0.15. Time increases from top to bottom for τ=0 to 60 in equal increments.

Figure 2. Conversion vs. distance profiles for varied γ and C; α=0.5. (a) γ=1.0, C=0.5; (b) γ=10, C=0.5; (c) γ=100, C=0.5; (d) γ=100, C=0.3;(e) γ=100, C=0.15. Time increases from bottom to top for τ=0 to 60 in equal increments.

Figure 3. Overpotential vs. distance profiles for varied γ and C; α=0.5. (a) γ=1.0, C=0.5; (b) γ=10, C=0.5; (c) γ=100, C=0.5; (d) γ=100, C=0.3;(e) γ=100, C=0.15. Time increases from bottom to top for τ=0 to 60 in equal increments.

Figure 4. Simulated chronoamperograms for varied γ and C. (a) γ varied at C=0.15; (b) C varied at γ=50.

Figure 5. Simulated current vs. $1/\sqrt{t}$ plots for varied γ and C. (a) γ varied at C=0.15; (b) C varied at γ=50.

Figure 6. Simulated chronocoulometric plots for varied γ and C. (a) γ varied at C=0.15; (b) C varied at γ=50.

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