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Reaction, diffusion and migration in conducting polymer electrodes: analysis of the steady-state amperometric response

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Abstract The processes of reaction, diffusion and electromigration of a charged substrate within an electronically conducting polymer film deposited on an inert supporting electrode are examined in terms of a quantitative analysis and solution of the pertinent differential equations. An analytical expression for the concentration profiles of substrate within the polymer layer is derived and a theoretical expression for the corresponding steady-state amperometric current response is presented. The transport and kinetics of the substrate are discussed in terms of a dimensionless reaction/diffusion parameter γ and a migration/diffusion parameter β.

Key words Conducting polymer electrodes · Amperometric chemical sensor · Mathematical modelling · Electroactive polymer · Heterogeneous redox catalysis

Introduction

The design, fabrication and application of novel amperometric chemical and biological sensors which use, as the active sensing element, electroactive polymer materials deposited as thin films on support electrode surfaces, has attracted considerable interest in recent years [1–3]. In recent work reported from our laboratory [4–6] we have indicated that modified electrodes fabricated from thin electrodeposited conductive polymer layers [e.g. poly(pyrrole)] exhibit good activity for the detection of ascorbic acid, catecholamines and quinones, when operated amperometrically. The detection potential is set at a value which enables facile oxidation of the analyte of choice. The value of the applied electrode potential is also such that the conducting polymer is in its oxidised electronically conducting state. This is an attractive situation from the analytical viewpoint since it is envisaged that the transfer of electrons through the polymer film should not be rate determining under these circumstances. Consequently the process of electronic communication between the underlying support electrode surface and the active sensing sites in the polymer film is optimised. Consequently for the oxidation of a substrate[1] species S to a product species P we can envisage the following bimolecular process:

$$\mathrm{S} + \mathrm{Pol}^{+} \xrightarrow{k} \mathrm{P} + \mathrm{Pol}$$

Here the substrate S reacts with oxidised sites Pol^{+} (polarons, bipolarons) located on the polymer chains, resulting in the generation of product species P and neutral polymer sites (Pol). Since the electrode potential is poised at a value such that the $\mathrm{Pol/Pol}^{+}$ reaction is favoured, one obtains a rapid regeneration of the oxidised site and so the substrate oxidation process is cyclic. A similar reaction may be written for the electroreduction of a substrate species. In this case we envisage the following bimolecular process:

$$\mathrm{S} + \mathrm{Pol} \xrightarrow{k} \mathrm{P} + \mathrm{Pol}^{+}$$

where substrate reacts with neutral sites located on the polymer chain.

A question immediately arises as to the location of the reaction site. Does the $\mathrm{S/Pol}^{+}$ reaction occur mainly at the polymer/solution interface, or does the bimolecular reaction occur within the bulk of the layer? This point is important since it will determine the degree to

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[1] In this paper we follow the biochemical convention and use the term substrate to represent the reactant species.

which the polymer film is utilised during the substrate/product transformation. The extent of permeability exhibited by an electrodeposited film will also depend to a large extent on the experimental conditions (e.g. choice of dopant counterion) employed during the process of electropolymerisation.

It is well established that some electronically conducting polymer materials are permeable to small molecules and ionic species [7]. For instance, Santhanam and O'Brien [8] demonstrated, using the method of laser interferometry, that poly(pyrrole) is porous and permeable to organic redox species. Previous work has indicated that poly(pyrrole) is permeable to H^{+}(aq), ferri/ferrocyanide ion, nitrobenzene and molecular oxygen [9–14]. The work of Schultze and co-workers [15] has indicated that poly(aniline) exhibits similar permeability to O_2 and H^{+}(aq). In contrast, Maksymiuk and Doblhofer [16] have shown, using the technique of rotating disc voltammetry, that thin films of poly(*N*-methylpyrrole) and poly(*N*-methylpyrrole)/poly(4-styrenesulfonate) are relatively impermeable to a range of inorganic ions such as $Fe(CN)_6^{3-/4-}$, $Ru(NH_3)_6^{3+/2+}$, Eu^{3+}/Eu^{2+}, $Co(en)_3^{3+/2+}$ and $Fe(C_2O_4)_3^{3-/4-}$. In this case the bimolecular redox reaction between substrate and reduced polymer site was shown to occur in a thin reaction layer of molecular dimensions at the polymer solution interface. The thickness of the reaction layer was estimated as $X_K = 10^{-7}$–10^{-8} cm. It was proposed by Maksymiuk and Doblhofer [16] that the lack of penetration into the polymer layer exhibited by the substrates examined was due to the rather rapid rate of reaction between the reduced poly(pyrrole) sites and the substrate species. This point is important. The balance between the rate of substrate diffusion within the layer and the rate of substrate chemical reaction at the polymer sites will determine the extent of penetration of the substrate into the layer and in turn will determine the spatial extent of layer utilisation in the substrate/product transformation. This point will be addressed in more detail later on in the paper.

Consequently, depending on the balance between diffusion and heterogeneous chemical kinetics, and on the morphology and permeability of the electrodeposited polymer, the bimolecular reaction between substrate and oxidised polymer (mediator) site can be located either at the polymer/solution interface or within the bulk of the thin film. The possibility of the mediator/substrate reaction being located at the support electrode/polymer interface should also not be discounted, especially if the polymer layer is very porous, if the substrate has a high mobility or if the reaction between the substrate and the mediator is sluggish. The various possibilities are presented in Fig. 1.

A further question arises. We can enquire as to the form of the kinetic law describing the interaction between the polymer site and the substrate. The answer to the latter question is not trivial. One useful analysis has been presented by Maksymiuk and Doblhofer [16]. In this approach the effect of the Donnan potential drop at the polymer/solution interface on the bimolecular electron transfer kinetics between substrate and oxidised site was examined. In an earlier communication [4] we proposed that the current response observed under steady-state batch amperometric conditions can be derived by solving the pertinent Fick diffusion equation modified by the addition of a chemical reaction term. Our experimental research programme [5, 6] has indicated that the form of the chemical reaction term can be complex. The available experimental data [5, 6, 17] suggest that, in a great majority of cases of mediated electrooxidation processes, the substrate partitions into and diffuses through the polymer layer and subsequently reacts at an

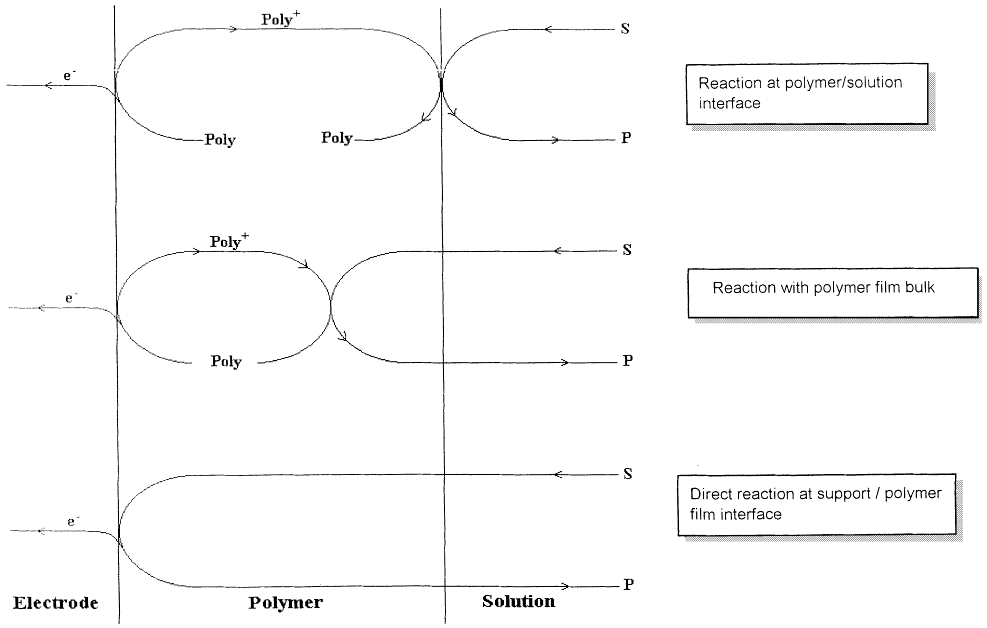

Fig. 1 Schematic representation of mediated electrocatalysis at a conducting polymer electrode material

oxidised polymer site. A specific binding interaction between substrate and polymer site is proposed. The complex formed via the latter interaction is assumed to decompose to form the product.

Hence we have postulated the following reaction mechanism:

$$\mathrm{S} + \mathrm{Pol}^{+} \xrightleftharpoons{K_\mathrm{m}} [\mathrm{SPol}]^{+}] \xrightarrow{k_\mathrm{c}} \mathrm{P} + \mathrm{Pol}$$

A detailed kinetic analysis of the latter sequence was shown [5, 6], to give rise to a characteristic biphasic current response when the bulk solution concentration of substrate was varied, under batch amperometric conditions. At low values of substrate concentration the observed steady-state current response increases linearly with increasing substrate concentrations. At high substrate concentrations the current response is independent of substrate concentration. At intermediate values of substrate concentration the current response varies in a non-linear yet regular manner with substrate concentration. This type of observation is well established in enzyme kinetics, where it is described in terms of the Michaelis-Menten mechanism [18]. Recently, Bartlett and co-workers have utilised and extended our analysis to describe the oxidation kinetics of NADH and poly(aniline) modified electrodes [19]. The reaction rate term for a Michaelis-Menten mechanism adopts the following form: $R(s) = k_\mathrm{c} c_\Sigma s / K_\mathrm{M} + s$, where s denotes the substrate concentration at any point within the polymer film, c_Σ denotes the concentration of oxidised polymer sites within the layer, and k_c and K_M denote the first order catalytic rate constant (which quantifies the kinetics of decomposition of the substrate/site complex) and the Michaelis constant (which provides a measure of the binding affinity between the polymer site and the substrate), respectively. If K_M is small, then the binding affinity between polymer site and substrate will be large.

We have shown that a complete analysis of reaction and diffusion within a conducting polymer film involves the solution of the following differential equation:

$$\frac{\partial s(x,t)}{\partial t} = D_\mathrm{S} \frac{\partial^2 s(x,t)}{\partial x^2} - \frac{k_\mathrm{c} c_\Sigma s(x,t)}{K_\mathrm{M} + s(x,t)} \tag{1}$$

Now chemical reaction and substrate diffusion are not the only processes which have to be considered when considering the amperometric response of conductive polymer sensors. As noted in the recent work of Doblhofer and Vorotyntsev [20], quite significant potential gradients can exist within conductive polymer thin films and one cannot simply assume that the potential gradients are uniform with distance within the film. Since many organic substrates (such as ascorbic acid) are ionised when they penetrate and react with polymer sites, it is reasonable to suppose that the substrate will migrate as well as diffuse in the polymer layer. Consequently the problem of reaction/diffusion/migration of a substrate through a thin polymer film will be addressed in some detail in the present communication.

It should be noted that the solution of diffusion/electromigration equations is of considerable interest in the area of ultramicroelectrode development. One major advantage exhibited by ultramicroelectrodes is that kinetic studies may be performed in media of low ionic strength. The quantitative analysis of such systems has been reported by Amatore et al. [22, 23] and by Oldham, Bond and co-workers [24–26].

Description of the boundary value problem

In this paper we consider a thin electronically conductive film deposited on the surface of an inert support electrode to form a chemically modified electrode. We assume that the layer is of a uniform thickness L. We further assume that the mediator sites (Pol^{+} and Pol for substrate oxidation and reduction, respectively) are uniformly dispersed throughout the bulk of the layer and that the polymer film is electronically conducting so that charge percolation from site to site throughout the polymer layer is not rate determining. We also, for the sake of simplicity, neglect the process of reactant or substrate diffusion in the Nernst diffusion layer immediately adjacent to the polymer/solution interface. In our kinetic work we utilise a rotating disc electrode and consequently concentration polarization of substrate in the diffusion layer can be specifically accounted for and the kinetic component of the observed current can be obtained via analysis using Koutecky-Levich plots [21]. Although the expression presented in Eq. 1 adequately describes the substrate reaction kinetics mediated via immobilized polymer sites, the inherent non-linearity of the Michaelis-Menten reaction term makes a full analytical solution of the differential equation difficult, especially when electromigration effects are also considered. Consequently, for the purposes of the present analysis we shall consider a more simple reaction rate term in which the substrate reaction kinetics are pseudo-first-order. Hence the reaction rate term is given by $R(s) = \frac{k_\mathrm{c} c_\Sigma}{K_\mathrm{M}} s = k\mathrm{s}$. This approximation will pertain when the substrate concentration within the film is very much less than the Michaelis constant K_M. Our analysis assumes pseudo-first-order kinetics and so we presume that the site concentration c_Σ remains constant. When measuring steady-state amperometric responses at conducting polymer electrodes, it is normal experimental practice to hold the electrode at a sufficiently oxidising potential that the mediator sites in the layer are entirely in their oxidised form at the electrode surface. Under such circumstances we can correctly neglect the process of charge percolation along the polymer strands since the latter process will be very rapid and not kinetically significant. Hence all sites in the layer will feel the influence of the applied potential to an equal extent and so the mediator Pol^{+} concentration will be uniform throughout the entire extent of the polymer film and the mediator concentration can be regarded as constant.

The situation becomes much more complex if charge percolation within the polymer is kinetically significant. This situation will be relevant if a redox polymer material is used as a detector electrode. In this case the reaction between the mediator site and the substrate will obey second-order kinetics and the analysis becomes significantly more complex. We shall address this more complex problem in a subsequent communication.

We shall also consider the more simple steady-state problem where the substrate concentration in the layer is not a function of time. Hence the time derivative of the substrate concentration within the layer may be set to zero. This simplification is especially valid if the rotating disc electrode is used to experimentally probe the substrate reaction kinetics.

We assume that the transport processes of diffusion and migration obey the Nernst-Planck equation[2] and so the electromigration term is given by the quantity $\frac{zFD_SE}{RT}\frac{\partial s}{\partial x} = \mu_S E\frac{\partial s}{\partial x}$, where z denotes the valence of the charged substrate, E denotes the electric field within the polymer film (which is assumed to be constant and independent of distance), μ_S denotes the mobility of substrate within the polymer and s represents the concentration of substrate in the layer.

We can then show that the pertinent reaction/diffusion/migration equation describing substrate transport and kinetics within the polymer film is given by:

$$D_S\frac{\mathrm{d}^2s}{\mathrm{d}x^2} - \frac{zFED_S}{RT}\frac{\mathrm{d}s}{\mathrm{d}x} - ks = 0 \tag{2}$$

This equation must be solved subject to the following boundary conditions: when $x = 0$, $\mathrm{d}s/\mathrm{d}x = 0$ and when $x = L$, $s = \kappa s^\infty$, where κ denotes the partition coefficient of the substrate and s^∞ denotes the bulk concentration of the substrate in solution. The first boundary condition implies that the substrate reacts on polymer sites and not on the support electrode surface, whereas the second boundary condition implies that the concentration polarization of the substrate in solution can be neglected.

To proceed further we recast the reaction/diffusion/migration equation presented in Eq. 2 into dimensionless form. This is done via definition of the following normalised parameters:

$$u = \frac{s}{\kappa s^\infty}, \quad \chi = \frac{x}{L}, \quad \gamma = \frac{kL^2}{D_S} = \frac{j_R}{j_D}, \quad \beta = \frac{\mu_S EL}{D_S} = \frac{j_M}{j_D} \tag{3}$$

where u represents a normalised substrate concentration ($0 < u < 1$) in the polymer film, χ is a normalised distance variable scaled to the total thickness of the polymer film (0, $\chi < 1$) and γ and β represent a normalised diffusion/reaction and diffusion/migration parameter, respectively. In fact the diffusion/reaction parameter γ is defined as the ratio of the flux due to chemical reaction to the flux arising from substrate diffusion through the polymer film. In a similar way the parameter β defines the ratio of the migration flux to the diffusion flux and compares the magnitudes of the transport rate of substrate through the film via migration and diffusion, respectively. Consequently the ratio γ/β compares the rate of substrate reaction at the polymer site to the rate of electromigration of substrate to the site.

Substituting Eq. 3 into Eq. 2 results in:

$$\frac{\mathrm{d}^2u}{\mathrm{d}\chi^2} - \beta\frac{\mathrm{d}u}{\mathrm{d}\chi} - \gamma u = 0 \tag{4}$$

This equation must be solved subject to:

$$\begin{aligned} &\chi = 0, \quad \frac{\mathrm{d}u}{\mathrm{d}\chi} = 0 \\ &\chi = 1, \quad u = 1 \end{aligned} \tag{5}$$

We now present a solution to the latter boundary value problem. The normalised steady-state current response y is given by:

$$y = \left(\frac{\mathrm{d}u}{\mathrm{d}\chi}\right)_{\chi=1} = \frac{iL}{nFAD_S\kappa s^\infty} \tag{6}$$

Hence in order to determine the steady-state current response y we must firstly integrate the differential equation presented in Eq. 4 subject to the boundary conditions outlined in Eq. 5.

Solution of the boundary value problem

The steady-state concentration profiles

We note that Eq. 4 is a second-order linear differential equation with constant coefficients, and consequently it may be integrated using standard methods. We assume a solution of the following form:

$$u(\chi) = \exp[\lambda\chi] \tag{7}$$

where λ must be determined. Substituting the latter expression and its derivatives into Eq. 4 we obtain the following characteristic equation:

$$\lambda^2 - \beta\lambda - \gamma = 0 \tag{8}$$

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[2] The latter statement is readily shown. The steady-state transport flux vector for any species i is given by:

$$\begin{aligned} \boldsymbol{j} &= -\frac{c_iD_i}{RT}\nabla\bar{\mu}_i = -\frac{c_iD_i}{RT}\nabla\{\mu_i + z_iF\psi\} \\ &= -\frac{c_iD_i}{RT}\nabla\bar{\mu}_i - \frac{z_iFD_ic_i}{RT}\nabla\psi \end{aligned}$$

Since $\boldsymbol{E} = -\nabla\psi$ then we obtain for the steady state flux:

$$\boldsymbol{j} = -D_i\nabla c_i + \frac{z_iFD_ic_iE}{RT}$$

Using the equation of continuity we then obtain that:

$$\frac{\partial c_i}{\partial t} = -\nabla\boldsymbol{j} = D_i\nabla^2c_i - \frac{z_iFD_ic_i\boldsymbol{E}}{RT}\nabla c_i$$

Simplifying to simple planar diffusion in one dimension, we obtain the expression for the electromigration contribution contained in the body of the paper.

This quadratic equation has two distinct roots given by:

$$\lambda = \frac{\beta \pm \sqrt{\beta^2 + 4\gamma}}{2} = \frac{\beta}{2} \pm \sqrt{\frac{\beta^2}{4} + \gamma} = \xi \pm \eta \tag{9}$$

where we define:

$$\begin{aligned} \xi &= \frac{\beta}{2} \\ \eta &= \sqrt{\gamma + \frac{\beta^2}{4}} = \sqrt{\gamma + \xi^2} \end{aligned} \tag{10}$$

The general solution to Eq. 4 is therefore given by:

$$u(\chi) = \exp[\xi\chi]\{A' \exp[\eta\chi] + B' \exp[-\eta\chi]\} \tag{11}$$

where A' and B' are integration constants which may be determined via analysis of the boundary conditions.

It is more convenient to recast Eq. 11 into the following format involving hyperbolic functions:

$$u(\chi) = \exp[\xi\chi]\{A \cosh[\eta\chi] + B \sinh[\eta\chi]\} \tag{12}$$

where $A = A' + B'$ and $A - B'$ are new integration constants. Differentiating Eq. 12 with respect to the space variable we obtain:

$$\begin{aligned} \frac{\mathrm{d}u}{\mathrm{d}\chi} &= A\xi \exp[\xi\chi] \cosh[\eta\chi] + A\eta \exp[\xi\chi] \sinh[\eta\chi] \\ &\quad + B\xi \exp[\xi\chi] \sinh[\eta\chi] + B\eta \exp[\xi\chi] \cosh[\eta\chi] \end{aligned} \tag{13}$$

Noting that $\mathrm{d}u/\mathrm{d}\chi = 0$ when $\chi = 0$ we can show from Eq. 13 that:

$$A = -\left(\frac{\eta}{\xi}\right) B \tag{14}$$

Also using the fact that $u = 1$ when $\chi = 1$ we obtain from Eq. 12 and Eq. 14 that:

$$B = \frac{\exp[-\xi]}{\sinh \eta - \left(\frac{\eta}{\xi}\right) \cosh \eta} \tag{15}$$

and so:

$$A = -\frac{\left(\frac{\eta}{\xi}\right) \exp[-\xi]}{\sinh \eta - \left(\frac{\eta}{\xi}\right) \cosh \eta} \tag{16}$$

Substituting the latter expressions into Eq. 12 we obtain the following expression for the normalised concentration profile of substrate through the polymer film:

$$u(\chi) = \frac{\left(\frac{\xi}{\eta}\right) \sinh[\eta\chi] - \cosh[\eta\chi]}{\left(\frac{\xi}{\eta}\right) \sinh \eta - \cosh \eta} \exp[-\xi(1 - \chi)] \tag{17}$$

When electric-field-induced electromigrational transport of the substrate species can be neglected, i.e. when the migration parameter $\beta \to 0$, then we can show that $\xi \to 0$, $\eta \to \sqrt{\gamma}$ as $\beta \to 0$ and so the concentration profile reduces to:

$$u(\chi) = \frac{\cosh[\sqrt{\gamma}\chi]}{\cosh\sqrt{\gamma}}$$

This expression has been derived in Eq. 10 of our previous communication [6]. We outline in Fig. 2 typical concentration profiles obtained using Eq. 17 for a range of β and γ values. Note that negative values of β imply a retardation in the rate of material transport owing to the presence of the electric field. The γ parameter is always positive.

In Fig. 2a the concentration profiles corresponding to a fixed γ value of 0.1 are presented. Hence the magnitude of the chemical reaction flux is one tenth that of the substrate diffusion flux. The concentration profiles corresponding to migration parameter values in the range -10 to $+10$ are presented. This corresponds to the range $-100 < \beta / \gamma < 100$. If we focus initially on the $\beta = 0$ case we see that for $\gamma = 0.1$ there is very little depletion of substrate throughout the bulk of the polymer film. Now we recall that when γ is small the substrate reaction flux is slower than the substrate diffusion flux, and we expect a rapid permeation of substrate through the entire layer followed by a small amount of chemical reaction which occurs throughout the entire film. Indeed we recall that $\sqrt{\gamma} = L/X_K$ where L denotes the layer thickness and X_{K} represents a characteristic reaction layer thickness which is defined as the distance the substrate travels in the layer before it undergoes chemical reaction with polymer sites. Hence for $\gamma = 0.1$, $\sqrt{\gamma} = L/X_K = 0.32$. The reaction layer thickness is considerably larger than the physical dimension of the layer. This is attributed to the rapid diffusion and slow rate of chemical reaction. When the migration parameter is finite and negative, the substrate concentration profiles indicate an even smaller amount of substrate depletion due to the fact that the field inhibits the transport of the charged substrate. On the other hand, when the migration parameter is finite and positive the electric field accelerates substrate transport and substantial substrate depletion is observed within the layer over and above that obtained for the simple reaction/diffusion case. Note for $\beta = 10$ the extent of substrate depletion is most marked in the region of the film near the film/solution interface.

In Fig. 2b the corresponding situation for $\gamma = 1$ is presented. Here $L = X_{\mathrm{K}}$ and the reaction layer thickness extends over the entire physical dimension of the polymer film. The concentration profile computed in the absence of electric field effects indicates a steady depletion of substrate through the layer. The concentration profiles computed for negative β values are relatively flat, again indicating very little substrate depletion due to chemical transformation within the film. However, the profiles observed for positive β values indicate a degree of substrate depletion considerably in excess of that observed in the absence of a field. When $\beta = 10$, virtually all of the substrate has undergone reaction at normalised distance values less than 0.5.

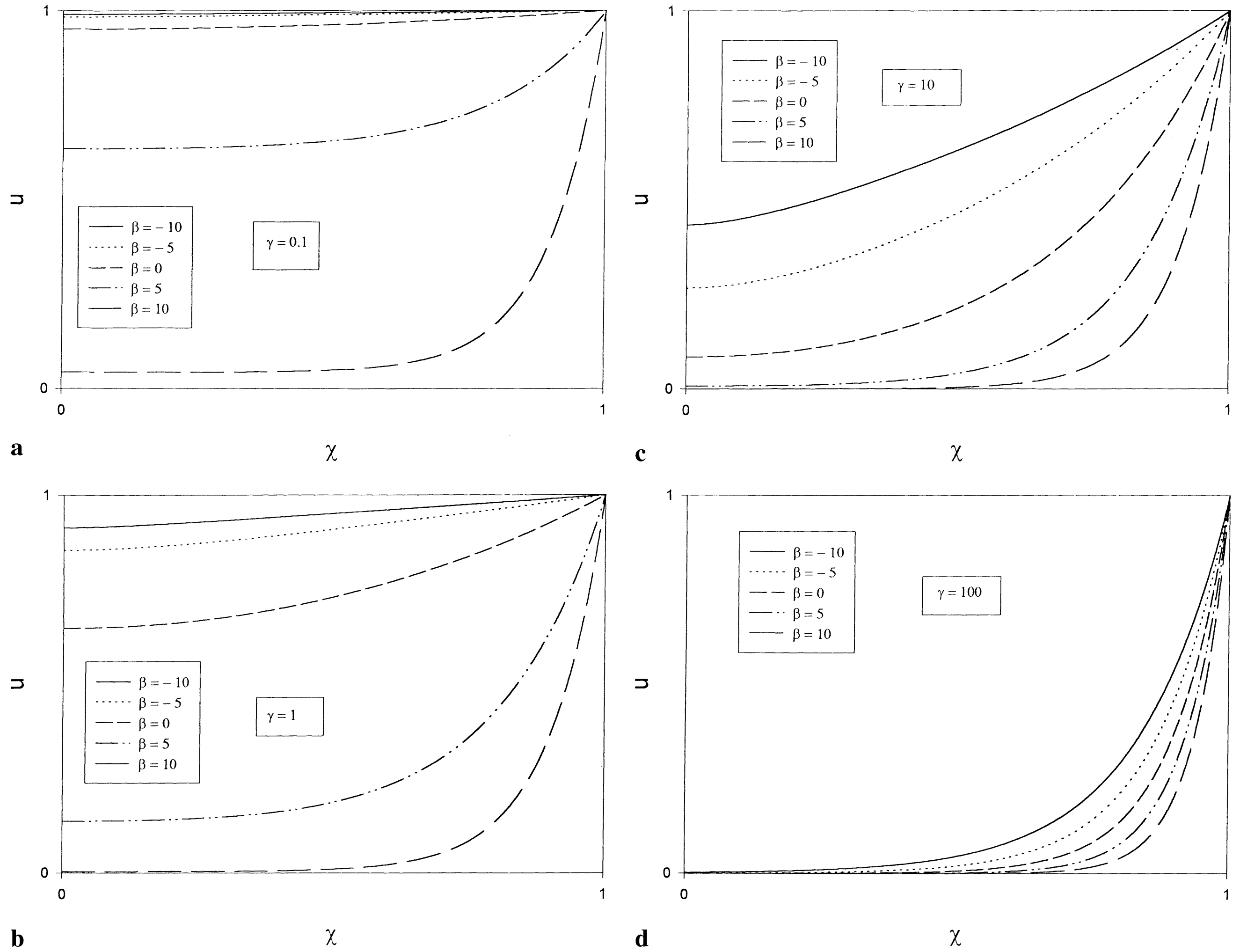

Fig. 2a–d Variation of normalised substrate concentration u with normalised distance χ for mediated electrocatalysis at a conducting polymer electrode. The concentration profiles are computed for four values of the reaction/diffusion parameter γ and for values of the migration parameter β in the range $-10 \leqslant \beta \leqslant 10$

The situation pertaining for $\gamma = 10$ is presented in Fig. 2c. Here $L/X_K = 3.2$ and so in the absence of electromigration effects we expect that the facility of the reaction kinetics between substrate and polymer site will be such that much of the substrate will undergo reaction before it has had a chance to diffuse far into the layer. If the applied electric field serves to inhibit substrate transport (negative β values), then we note from the more shallow nature of the concentration profiles that there is considerably less substrate depletion than that observed for the zero β situation. The opposite pertains for the cases of positive β.

The situation pertaining for large γ values is presented in Fig. 2d. Here $L/X_K = 10$ and the rate of chemical reaction is considerably faster than that of diffusion. Hence much of the substrate is consumed in a first-order reaction layer near the polymer/solution interface. The magnitude and sign of the migration parameter β have only a small effect on the shape of the concentration profile.

It is instructive to use Eq. 17 to evaluate u_0 the normalised concentration of substrate present in the steady-state at the support electrode/polymer interface. The results of such a calculation are presented in Fig. 3, where u_0 is plotted as a function of the migration parameter β for four values of the reaction/diffusion parameter γ. When γ is small, the rate of chemical reaction is much slower than the rate of substrate diffusion. Hence u_0 remains close to unity for β values between -10 and 0. However, u_0 subsequently drops rapidly to values near zero when there is a positive electromigrative contribution to the substrate transport and kinetics. This observation implies that the local electric field in the film serves to enhance the rate of chemical transformation of the substrate to the product, and indeed, when considered along with the shape of the concentration profiles presented in Fig. 2a, also indicates that when β is large and positive, much of the layer remains un-utilised in the chemical reaction. Indeed the enhancement of the chemical reaction flux under the latter conditions is such that the β term practically negates the low γ value. A similar u_0 versus β trend is observed for larger γ values.

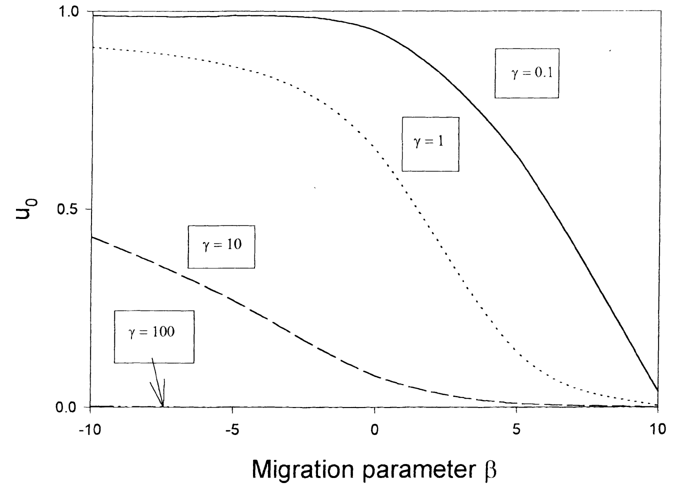

Fig. 3 Variation of substrate concentration at the support electrode/polymer interface as a function of migration parameter β for different values of the reaction/diffusion parameter γ

The value of u_0 drops appreciably as γ is increases (as it should), and u_0 also decreases sharply with increasingly more positive β value.

The steady-state current response

We now evaluate the analytical form of the normalised steady-state current response. To achieve this we use Eq. 6, note the values of the integration constants A and B from Eq. 15 and Eq. 16, and set $\chi = 1$ in Eq. 13 to obtain:

$$y = \frac{\left(\xi - \frac{\eta^2}{\xi}\right)\tanh\,\eta}{\tanh\,\eta - \left(\frac{\eta}{\xi}\right)} \tag{19}$$

The latter expression may be rearranged into a more transparent form by noting that $\xi - \frac{\eta^2}{\xi} = -\frac{2\gamma}{\beta}$ and $\frac{\eta}{\xi} = \frac{2}{\beta}\sqrt{\gamma + \frac{\beta^2}{4}}$. Substituting the latter expressions into Eq. 19 and simplifying produces:

$$y = \frac{2\gamma\tanh\sqrt{\gamma + \frac{\beta^2}{4}}}{\sqrt{4\gamma + \beta^2} - \beta\tanh\sqrt{\gamma + \frac{\beta^2}{4}}} = \frac{\gamma\tanh\sqrt{\gamma + \frac{\beta^2}{4}}}{\sqrt{\gamma + \frac{\beta^2}{4}} - \frac{\beta}{2}\tanh\sqrt{\gamma + \frac{\beta^2}{4}}} \tag{20}$$

This is the general expression for the steady-state current response. When $\beta = 0$ we note that Eq. 20 reduces to:

$$y = \sqrt{\gamma}\tanh\sqrt{\gamma} \tag{21}$$

The latter result is in agreement with an expression derived in our previous paper [6].

We illustrate Eq. 20 in Fig. 4a where we present a plot of normalised current response y as an explicit function of the migration parameter β for various values of the reaction/diffusion parameter γ. We note that for a given value of γ the normalised current increases with increasing value of the migration parameter β. In Fig. 4b we present a log/log plot of normalised current as a function of reaction/diffusion parameter γ for various values of the migration parameter β. The shape of the plot changes as the value of the migration parameter varies from large negative values to large positive values. For instance, for $\beta = 0$ the plot of log y versus log γ exhibits a clear "dog leg" form with the slope changing from unity to 0.5 with increasing γ value. This behaviour can be readily understood as follows. For instance, when $\beta = 0$ we note that Eq. 21 predicts that when γ is small $\tanh\sqrt{\gamma} \approx \sqrt{\gamma}$ and so $y \approx \gamma$ and the log/log plot should exhibit a slope of unity. On the other hand, when γ is large we note that $\tanh\sqrt{\gamma} \approx 1$ and $y \approx \sqrt{\gamma}$ and the slope of the double logarithmic plot should be 0.5. This is indeed as observed in Fig. 4b.

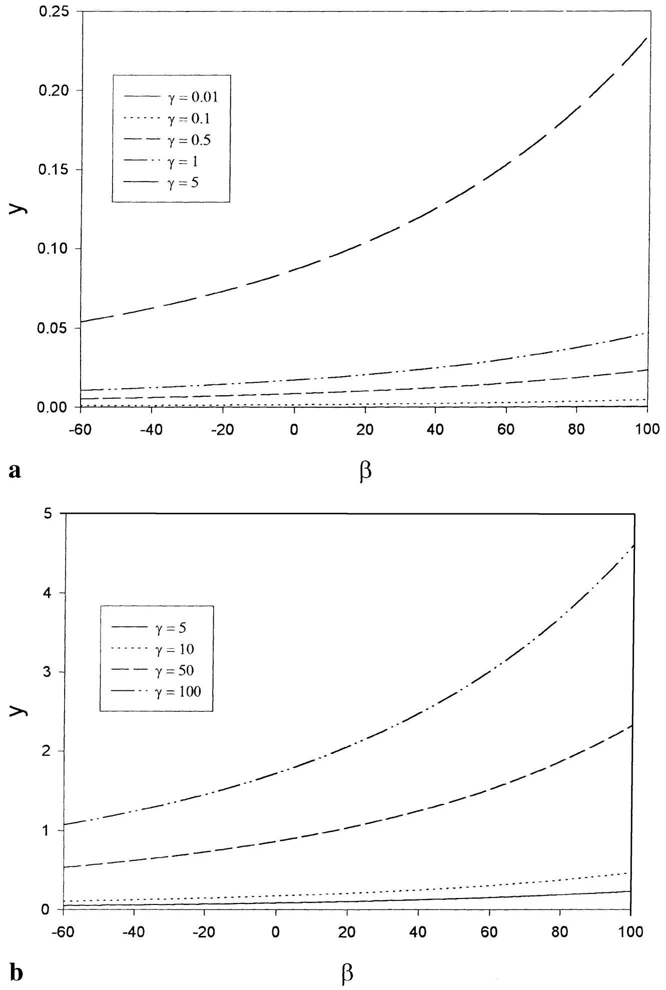

Fig. 4 **a** Variation of normalised steady-state current response with migration parameter β. Data are presented for the region of small and large γ values. **b** Double logarithmic plot illustrating the variation of normalised current with reaction/diffusion parameter γ for a wide range of β values

The situation is more complicated when the migration parameter is finite. For instance, if we assume that the reaction/diffusion parameter is large and that $\gamma \gg \beta^2/4$ or $\sqrt{\gamma} = L/X_K \gg \beta/2$ then we can assume that $\tanh\sqrt{\gamma + \beta^2/4} \approx \tanh\sqrt{\gamma}$ and so the current response presented in Eq. 20 reduces to:

$$y \approx \frac{2\gamma \tanh\sqrt{\gamma}}{2\sqrt{\gamma} + \beta \tanh\sqrt{\gamma}} \tag{22}$$

Now since $\sqrt{\gamma}$ is large we can assume that $\tanh\sqrt{\gamma} \cong 1$ and so Eq. 22 reduces to:

$$y \cong \frac{2\gamma}{2\sqrt{\gamma} + \beta} = \frac{\sqrt{\gamma}}{1 + \frac{\beta}{2\sqrt{\gamma}}} \xrightarrow{\gamma \text{ large, } \beta \text{ small}} \sqrt{\gamma} \tag{23}$$

Hence when $\sqrt{\gamma}$ is large we note from Eq. 23 that the normalised current response should increase with $\sqrt{\gamma}$ but that the rate of increase is moderated by the electric-field-dependent factor $\left(1 + \frac{\beta}{2\sqrt{\gamma}}\right)^{-1}$

In contrast, when $\sqrt{\gamma} \ll \beta/2$ we can assume that $\sqrt{\gamma + \beta^2/4} \approx \beta/2$ and so the current response reduces to:

$$y \approx \frac{2(\gamma/\beta)\tanh\left[\frac{\beta}{2}\right]}{1 + \tanh\left[\frac{\beta}{2}\right]} \tag{24}$$

In this case the hyperbolic functions involve the migration parameter alone. Now if the migration parameter is very large and the diffusion/reaction parameter small, then $\tanh[\beta/2] \cong 1$ and Eq. 24 reduces to:

$$y \cong 2\beta^{-1}\gamma \tag{25}$$

If the migration parameter is small but the diffusion/reaction parameter is still smaller, then we can write $\tanh[\beta/2] \cong \beta/2$ and Eq. 24 reduces to:

$$y \cong \left(1 + \frac{\beta}{2}\right)^{-1}\gamma \tag{26}$$

Specifically for the range $-1 < \beta/2 < 1$ we note that $(1 + \beta/2)^{-1} \cong 1 - \beta/2$ and so Eq. 26 simplifies still further to:

$$y \cong \left(1 - \frac{\beta}{2}\right)\gamma \xrightarrow{\beta \to 0} \gamma \tag{27}$$

Hence for small values of γ we predict that the normalised current response y should vary linearly with the reaction/diffusion parameter γ, but the rate of this variation will depend on the field-dependent factor $(1 + \beta/2)^{-1}$.

When the latter limiting forms of Eq. 20 are considered, then it is not surprising that the simple "dog leg" behaviour exhibited by the $\beta = 0$ situation is not observed for finite non-zero β values. The slope of unity is observed over most of the range of γ values examined when β is negative. However, when β is finite and slightly positive the unity slope region in the double logarithmic plot is observed only over a more restricted range of γ values. When β is large and positive, very little variation of normalised current y with reaction/diffusion parameter γ is observed.

We can obtain a further insight into the transport and kinetics by comparing selected critical values of the flux ratio parameter $\beta/\gamma = j_M/j_R$ with selected values of the reaction/diffusion parameter $\gamma = j_R/j_D$. This exercise results in the construction of a schematic case diagram which is presented in Fig. 5. For all values of β/γ and when γ is large the reaction is diffusion controlled. In the upper-right hand quadrant the electromigration flux will typically be larger than the reaction flux and both will be much larger than the flux due to substrate diffusion. In the lower-right hand quadrant the reaction flux will be much larger than the electromigration flux, which is turn will be much larger than the diffusion flux. Both of these situations are designated case D. In contrast, in the upper left-hand quadrant when β/γ is large and when γ is small, the net reaction rate (or current) will be controlled by a slow rate-determining chemical reaction. This is designated case R. In this quadrant the electromigration flux is greatest. In the lower left-hand quadrant when β/γ is small and when γ is small, the net current will be governed by the electromigration flux. This is case M. Here the flux due to substrate diffusion will be largest. In the region close to the origin of the coordinate system, the general case DMR applies where $\beta/\gamma = \gamma = 1$. In this region the current will be equally determined by each of the underlying processes.

Concluding comments

The effect of substrate electromigration within an electrodeposited electroactive polymer thin film sensor, on

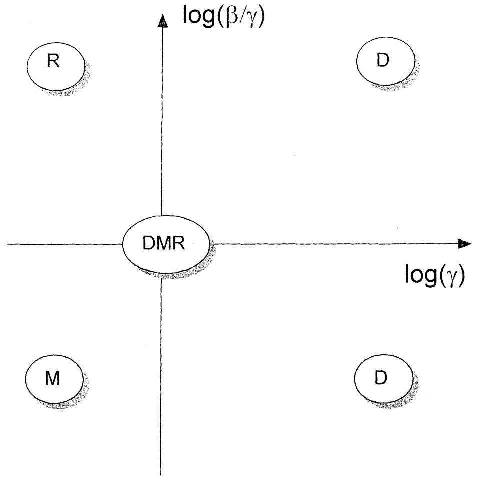

Fig. 5 Schematic case diagram illustrating the possible rate-determining steps as a function of the parameters β/γ and γ

the shape of both the steady-state substrate concentration profiles and the steady-state amperometric current response, has been elucidated via the analytical solution of the governing reaction/diffusion migration differential equation. The electromigration effect has been quantified in terms of a parameter β which depends on the magnitude of the electric field strength within the polymer film. The β parameter represents the ratio of the migration flux to the diffusion flux. The effect of the internal electric field will be most apparent when the reaction/diffusion parameter γ is small (the γ parameter reflecting the ratio of the chemical reaction flux to the diffusion flux). Hence electromigration will be relatively unimportant when the rate of chemical reaction is large compared to the rate of substrate diffusion. Under such circumstances the mediated reaction takes place in a reaction layer at the polymer/solution interface, which is of molecular dimension.

The present analysis is also restricted in scope in that we only consider the situation where the reaction kinetics are first order in substrate concentration. Consequently the analysis will only be valid for situations where the substrate concentration in the film will be less than the Michaelis constant K_M. Under such conditions we expect that the layer will be unsaturated, i.e. not all polymer active sites will be occupied by substrate. We are currently examining the more complicated situation where a certain degree of site saturation exists in the layer.

We are also extending the analysis to consider the more complex situation of the time-dependent amperometric current response exhibited by a conducting polymer electrode and the situation of reaction/diffusion/migration within a free-standing polymeric membrane material.

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