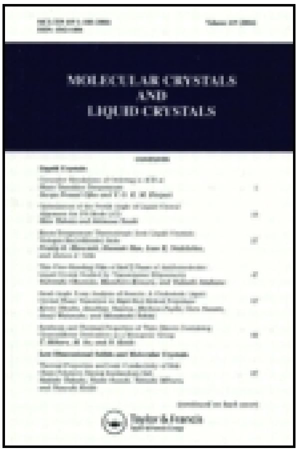

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IMPEDANCE ANALYSIS OF THE KINETICS OF ELECTROCHEMICAL PROCESSES MEDIATED BY POLYMER LAYERS

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Abstract. A kinetic model for the interpretation of the impedance of reactions occurring on polymer modified electrodes is presented, which is based on the description of the electron exchange process by a chemical reaction. The limiting case of a surface reaction is examined in detail.

INTRODUCTION

Redox and conductive polymer films have been extensively studied as electrocatalytic thin-layer materials with the aim of improving electrode performance for possible synthesis or analytical purposes.

Several factors complicate the kinetic analysis of electrochemical reactions occurring at polymer modified electrodes :

- the presence of two interfaces (metal/polymer, polymer/electrolyte),
- the occurrence of the electron exchange reaction over a variable depth of the polymer film,
- the yet unclear nature of charge transport in polymer films.

We have earlier presented a calculation of the ac and EHD impedance of a mediated reaction occurring exclusively at the polymer-electrolyte interface, based on the assumption that the electron exchange reaction could be split in two electrochemical half reactions [1] . We examine here the possibility of calculating the ac impedance of the same system by describing electron exchange by a chemical reaction and charge transport by electron hopping. Such an approach has, in principle, the advantage that it may be extended to situations in which electron exchange occurs over any depth from 0 to the whole film thickness ϕ (including direct reaction on the metal).

In this paper, the calculation for a very fast electron exchange is presented, i.e. the limiting case of surface reaction already examined in ref.1.

MODEL

The polymer contains fixed redox centres, either reduced (P) or oxidized (Q), and is permeated by the electrolyte so that, in the absence of any currrent the substrate Ox/Red is present at all x at its bulk concentration.

At the metal-polymer interface both couples may undergo electrochemical reaction following Butler-Volmer kinetics :

$$i_{P/Q} = C_P(o)\, k_{f1} \exp \frac{\alpha_1 F}{RT} \eta - C_Q(o)\, k_{b1} \exp - \frac{(1-\alpha_1)F}{RT} \eta$$

(1)

$$i_{Red/Ox} = C_{Red}(o)\, k_{f2} \exp \frac{\alpha_2 F}{RT} \eta - C_{Ox}(o)\, k_{b2} \exp - \frac{(1-\alpha_2)F}{RT} \eta \qquad (2)$$

where η is the electrode potential measured with respect to the equilibrium potential of Ox/Red.

Gradients of both polymer and substrate redox centres are given by :

$$i = i_{P/Q} + i_{Red/Ox} = F\,(D_E \frac{\partial C_P}{\partial x}\Big|_o + D_f \frac{\partial C_{Red}}{\partial x}\Big|_o) \qquad (3)$$

where D_E is the so-called diffusion coefficient of electrons, and D_f the diffusion coefficient of Red/Ox in the film.

In the polymer film, electron transport by hopping and chemical reaction between P/Q and Red/Ox occur, so that :

$$\frac{\partial C_P}{\partial t} = - K_F C_P C_{Ox} + K_B C_Q C_{Red} + D_E \frac{\partial^2 C_P}{\partial x^2} \qquad (4)$$

$$\frac{\partial C_{Ox}}{\partial t} = - K_F C_P C_{Ox} + K_B C_Q C_{Red} + D_f \frac{\partial^2 C_{Ox}}{\partial x^2} \qquad (5)$$

STEADY-STATE

In the most general case both $i_{P/Q}$ and $i_{Red/Ox}$ are not zero. However, effective mediation is only obtained when all Red/Ox reacts with P/Q, not with the underlying metal, i.e. for $i_{Red/Ox} = 0$

In the other extreme situation, Red/Ox reacts without mediation : $i = i_{Red/Ox}$. This behaviour may be observed either because the polymer is not electroactive (k_{f1} and $k_{b1} \to 0$) or the exchange reaction is infinitely slow (K_F and $K_B \to 0$).

For $i_{Red/Ox} = 0$, one may calculate the steady-state current, using the following boundary conditions :

- for x = 0 : $\frac{\partial C_{Ox}}{\partial x} = 0$

- for $x = \phi$: $\quad \frac{i}{F} = -D_f \frac{\partial C_{Ox}}{\partial x} \quad ; \quad \frac{\partial C_P}{\partial x} = 0$

The stationary concentration profile of C_{Ox} becomes :

$$C_{Ox}(x) = \frac{C_\infty}{\cosh\frac{\phi}{x_r}} \; \frac{\frac{K_FC_P - K_BC_Q}{K_FC_P + K_BC_Q}}{1 + \frac{D_f\delta}{x_rD_s}\tanh\frac{\phi}{x_r}} \; \cosh\frac{x}{x_r} + \frac{2C_\infty K_BC_Q}{K_FC_P + K_BC_Q} \qquad (6)$$

where : $x_r = \sqrt{\frac{D_f}{K_FC_P + K_BC_Q}}$ is the depth over which a net exchange reaction occurs, D_S the diffusion coefficient of Red/Ox in solution and δ the diffusion layer thickness..

By integrating Eq. (3) and substituting the C_{Ox} expression, one obtains $C_P(x)$. The C_{Ox} and C_P profiles are given in Fig. 1 which shows that current is mainly transported by P/Q (i.e. electrons) for $x < \phi - x_r$ and by Red/Ox for $x > \phi - x_r$. For a thin reaction layer one obtains ($x_r << \phi$) :

$$C_{Ox}(o) = \frac{2C_\infty K_BC_Q}{K_FC_P + K_BC_Q} \qquad (7)$$

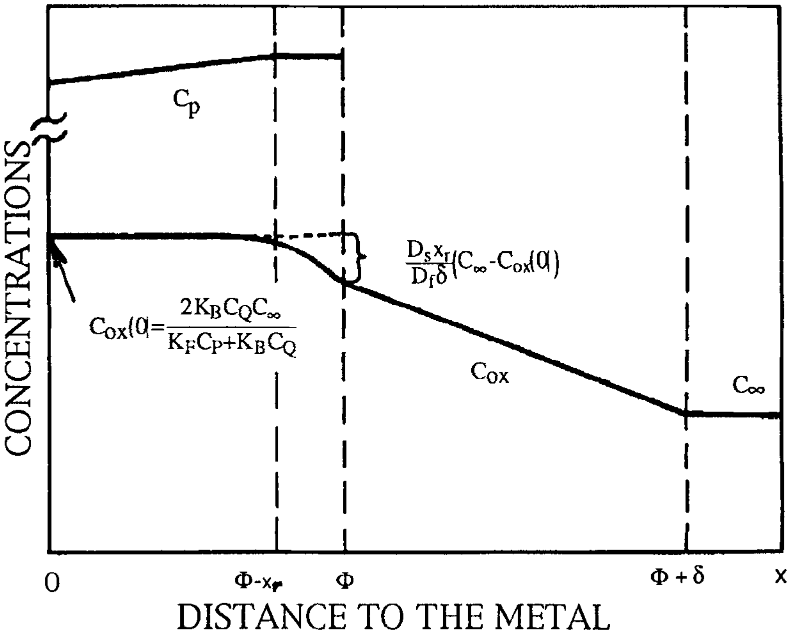

FIGURE 1 : Schematic representation of the stationary concentration profiles of Ox and P.

and :
$$C_{Ox}(\phi) = C_{Ox}(o) + \frac{D_s x_r}{D_f \delta}\left(C_\infty - C_{Ox}(o)\right) \qquad (8)$$

The faster is the mediation reaction, the thinner is x_r and the smaller the difference between $C_{Ox}(\phi)$ and $C_{Ox}(o)$.

The steady-state i-E curve becomes :

$$i = -\frac{FD_s C_\infty}{\delta}\,\frac{1 - \exp\frac{F}{RT}\eta}{1 + \exp\frac{F}{RT}\eta} + \frac{FD_s}{\delta}\left(C_\infty - C_{Ox}(o)\right)\frac{D_s x_r}{D_f \delta} \qquad (9)$$

For $x_r \rightarrow 0$, the i-E curves approach that typical of an infinitely fast process, whatever is the value of k_{f2} and k_{b2}, i.e. irrespective of the fact that the direct reaction of Red/Ox on a bare electrode is fast or slow. Instead, when x_r is not negligible, the absolute value of i is somewhat lower at all E.

IMPEDANCE

Of the two situations leading to no-mediated reaction the one involving electrochemical processes occurring at electrodes coated with inert polymer layers has been previously treated [2]. On the other hand, for an electroactive polymer unable to exchange electrons with Red/Ox (K_F and $K_B \approx 0$), the transient current is the sum of the currents due to Red/Ox reaction ($\tilde{i}_{Red/Ox}$) and the charge-discharge of the film ($\tilde{i}_{P/Q}$). Thus the overall impedance is the parallel combination of the impedance of the Red/Ox reaction occurring at a coated electrode [2] and that of the film in an inert electrolyte [3].

Much more interesting is the case of effective mediation for which $\bar{i}_{Red/Ox} = 0$. It is worth noting that $\bar{i}_{Red/Ox} = 0$ does not mean $\tilde{i}_{Red/Ox} = 0$. However, in the present paper x_r is assumed to be vanishingly small ; for $C^* >> C_\infty$, this leads to $\tilde{i}_{Red/Ox} << \tilde{i}_{P/Q}$.

The ac impedances are calculated by assuming that i and E undergo sinusoidal variations, so that, e.g. :

$$E = \bar{E} + \mathrm{Re}\,(\tilde{E}\exp j\omega t) \qquad (10)$$

By differentiating Eq. (1) :

$$\tilde{i} = \tilde{i}_{P/Q} = A_1 \tilde{C}_P(o) + R_t^{-1}(\tilde{E} - R_E\tilde{i}) \qquad (11)$$

where :
$$A_1 = k_{f1}\exp\frac{\alpha_1 F}{RT}\eta + k_{b1}\exp - \frac{(1-\alpha_1)F}{RT}\eta \qquad (12)$$

$$R_t^{-1} = \frac{F}{RT}\left[\,\alpha_1 k_{f1} C_P(o)\exp(\alpha_1 F\,\bar{E}/RT) + (1-\alpha_1)k_{b1}C_Q(o)\exp - (1-\alpha_1)F\,\bar{E}/RT\,\right] \tag{13}$$

R_E is the uncompensated electrolyte resistance.

Under the assumption that the exchange reaction is at quasi-equilibrium for $0 \le x \le \phi\text{-}x_r$:

$$\tilde{C}_P(x) = -\,\frac{K_F\bar{C}_P + K_B\bar{C}_Q}{K_F\bar{C}_{Ox} + K_B\bar{C}_{Red}}\;\tilde{C}_{Ox}(x) \tag{14}$$

and from Eq. (4) transient charge transport in the film is described by :

$$j\,\omega\,\tilde{C}_P = D_E\,\frac{\partial^2\tilde{C}_P}{\partial x^2} \tag{15}$$

as in ref.1.

This leads to :

$$\tilde{C}_P(x) = M\exp\,(j\omega x^2/D_E)^{1/2} + N\exp - ((j\omega x^2/D_E)^{1/2} \tag{16}$$

One of the two boundary conditions needed to compute M and N is the same as in ref.1 :

$$\tilde{i} = FD_E\,\frac{\partial\tilde{C}_P}{\partial x}\Big|_o \tag{17}$$

The other one is obtained from the definition of a dimensionless convective diffusion impedance [4] :

$$\frac{\partial\tilde{C}_{Ox}}{\partial x}\Big|_\phi = \frac{\tilde{C}_{Ox}(\phi)}{\delta}\,\theta'_o \tag{18}$$

Considering that the transient currents of electroactive species are due to P/Q in $x = \phi - x_r$ and to Red/Ox in $x = \phi$, one has :

$$D_E\,\frac{\partial\tilde{C}_P}{\partial x}\Big|_{\phi\text{-}x_r} = -\,D_s\,\frac{\partial\tilde{C}_{Ox}}{\partial x}\Big|_\phi \tag{19}$$

(This assumption is the more valid as x_r is smaller).

By combining Eqs (14), (18) and (19), one obtains :

$$FD_E\,\frac{\partial\tilde{C}_P}{\partial x}\Big|_{\phi\text{-}x_r} = FD_s\,\frac{K_F\bar{C}_P + K_B\bar{C}_Q}{K_F\bar{C}_{Ox} + K_B\bar{C}_{Red}}\;\frac{\tilde{C}_P(\phi)}{\delta}\,\theta'(o) \tag{20}$$

which may be used as a boundary condition in $x = \phi$, since $x_r \ll \phi$.

By computing M and N and substituting $\tilde{C}_P(o) = M + N$ in Eq. (11), the ac impedance becomes :

$$\frac{\tilde{E}}{\tilde{i}} = R_E + R_t + \frac{Z_D + \dfrac{1}{C_{LF}}\dfrac{\phi^2}{D_E}\dfrac{\tanh s_1^{1/2}}{s_1^{1/2}}}{1 + Z_D C_{LF}\dfrac{D_E}{\delta^2} s_1^{1/2} \tanh s_1^{1/2}} \qquad (21)$$

where $C_{LF} = F\phi/A_1R_t$ is the polymer redox capacitance, $s_1 = j\omega\phi^2/D_E$, and Z_D is the convective diffusion impedance for an infinitely fast reaction.

Eq. (1) has the same form as the ac impedance expression given in ref. [1], except that charge transfer resistances relative to the polymer/electrolyte interface cannot appear here.

Examples of simulated impedance diagrams are shown in Fig. 2. They reproduce the diagrams experimentally observed for some redox and conducting polymers [5,6,7].

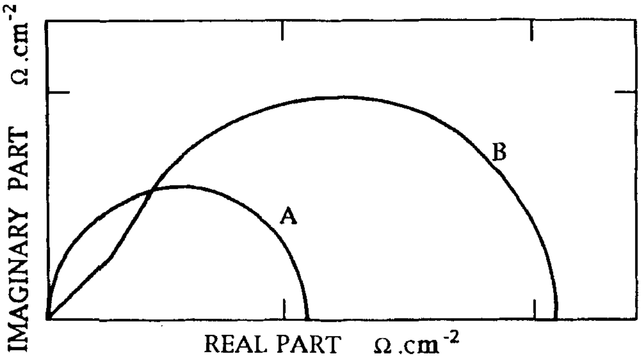

FIGURE 2 : Ac impedance calculated according to Eq. (21) with $Z_D(\omega=0) = 100\ \Omega$, $C_{LF} = 10^{-2}$F, $R_t = 0\ \Omega$, $\phi^2/D_E = 10^{-6}$ s (A), 1s (B).

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