

Impedance analysis of electrodes modified with a reversible redox polymer film

C. GABRIELLI¹, O. HAAS², H. TAKENOUTI¹

¹*LP 15 du CNRS, 'Physique des Liquides et Electrochimie', Université Pierre et Marie Curie, Tour 22, 4 place Jussieu, 75252 Paris Cedex 05, France*

²*Swiss Federal Institute for Reactor Research CH-5303 Würenlingen, Switzerland*

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The study of the kinetics of an electrode coated with a redox polymer film has been carried out using an impedance technique. A theoretical model is proposed which takes into account the diffusion of the active centres. Experimental results are presented for a glassy carbon electrode coated with a [Ru(bpy)₂ poly(4'-vinylpyridine)C1]Cl film. There is good agreement between these results and the model.

1. Introduction

Although a large number of publications [1–7] have been devoted to the kinetic characterization of electrochemical reactions mediated by redox polymer films, it seems that impedance techniques have been little used for this purpose [8]. The classical technique in these studies is linear sweep voltammetry coupled with chronoamperometry. The latter is used in order to determine the characteristic transport time of the charge within the film. Impedance analysis, however, is now well established for the investigation of reaction mechanisms at metal–electrolyte interfaces. The electrochemical parameters can be evaluated even for complex couplings between interfacial reactions and mass transport. Hence a study of the kinetics of electrodes coated with a redox polymer film has been attempted using an impedance technique.

In this paper we present a theoretical treatment along with measurements of a system consisting of a redox polymer film, namely [Ru(bpy)₂ poly(4'-vinylpyridine)C1] Cl [9] on a glassy carbon electrode in 1 M HCl having no electrochemically active redox couple (substrate) in solution.

2. Model description

Several models have been suggested to describe the kinetics of modified electrodes under steady-state conditions with a substrate in solution [1–7]. To interpret the simple case with no substrate in solution we need only consider the charge transfer at the electrode polymer interface and the charge transport within the polymeric film.

The charge transport in the film is understood to be a diffusion-like process. Since the redox centres are fixed to the polymer they are not able to diffuse in a proper way, even though these centres may have a certain mobility. By mutual electron transfer between two adjacent redox centres, however, a charge transport through the entire film is possible without significant displacement of the redox centres themselves (Fig. 1). This charge transport obeys Fick's law where the diffusion coefficient depends not only on the electron exchange rate (self-exchange rate) between the redox centres but also on the diffusion of these centres themselves. In general this charge transport process is accompanied by counter-ion diffusion which assures electroneutrality throughout the film. The charge transport within the film depends, therefore, on the counterion diffusion in the film, the self-exchange rate of the redox centres and the mobility of the polymer 'fixed' redox centres.

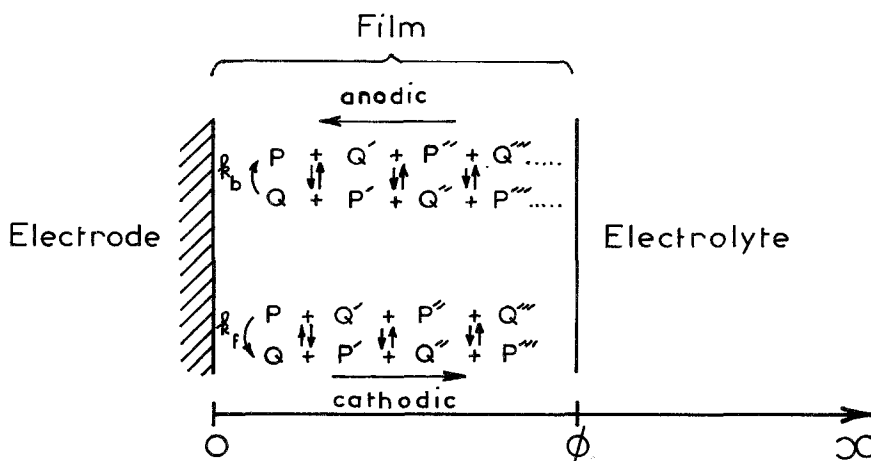


Fig. 1. Scheme of the electrode–film–electrolyte system studied. ϕ = Thickness of the polymer film.

Using the notation of Andrieux *et al.* [1] the electroactive centres P and Q correspond in our case to Ru(III) and Ru(II) centres in the film. These centres are supposed to be uniformly distributed in the film of thickness, ϕ , placed at the surface of a glassy carbon disc electrode.

The charge transport through the film which Saveant often calls ‘diffusion’ of electrons, is governed by the equations

$$\frac{\partial C_Q}{\partial t} = D_E \frac{\partial^2 C_Q}{\partial x^2}, \quad \frac{\partial C_P}{\partial t} = D_E \frac{\partial^2 C_P}{\partial x^2} \quad (1)$$

where C_Q , C_P are the concentrations of Q and P, and D_E is the ‘diffusion’ coefficient for this charge transport.

The electroactive centres, P and Q, may exchange electrons with the electrode at the electrode–film interface:



where the total concentration of the redox couple is

$$C_P + C_Q = C^* \quad (3)$$

Reaction 2 leads to the faradaic current

$$I_F = FA [k_f C_P - k_b C_Q] \quad (4)$$

where F is the Faraday constant, A the surface area of the electrode, and k_f and k_b are respectively the forward and backward reaction rates which follow the Tafel law.

$$k_f = k_f^0 \exp b_f E \quad (5)$$

$$k_b = k_b^0 \exp (-b_b E) \quad (6)$$

where b_f and b_b are the Tafel coefficient:

$$b_f = \frac{\alpha F}{RT} \quad \text{and} \quad b_b = \frac{(1 - \alpha)F}{RT}$$

and α , R and T have their usual meanings.

The boundary condition for Fick's law (1) at the electrode surface ($x = 0$) is given by:

$$I_F = FAD_E \left. \frac{\partial C_P}{\partial x} \right|_0 = -FAD_E \left. \frac{\partial C_Q}{\partial x} \right|_0 \quad (7)$$

At the film-electrode boundary ($x = \phi$) the redox centres P and Q are unable to leave the film. Therefore the concentration gradients vanish:

$$\left. \frac{\partial C_Q}{\partial x} \right|_\phi = \left. \frac{\partial C_P}{\partial x} \right|_\phi = 0 \quad (8)$$

For this system the static and dynamic behaviours are now discussed in turn.

2.1. Steady state

The steady-state behaviour is obtained by setting $d/dt \equiv 0$. It then follows from Equation 1:

$$\frac{\partial^2 C_Q}{\partial x^2} = \frac{\partial^2 C_P}{\partial x^2} = 0 \quad (9)$$

and

$$\frac{\partial C_Q}{\partial x} = \text{cte}; \quad \frac{\partial C_P}{\partial x} = \text{cte} \quad (10)$$

However, the boundary conditions at $x = \phi$ (Equation 8) require that

$$\frac{\partial C_Q}{\partial x} = \frac{\partial C_P}{\partial x} = 0 \quad (11)$$

It follows that $C_Q = \text{cte}$ and $C_P = \text{cte}$, and hence do not depend on x , throughout the film.

From Equations 4, 7 and 11 one gets:

$$I_F = 0 \quad (12)$$

and

$$k_f C_P = k_b C_Q$$

As $C_P = C^* - C_Q$

$$C_Q = \frac{k_f C^*}{k_f + k_b} \quad \text{and} \quad C_P = \frac{k_b C^*}{k_f + k_b} \quad (13)$$

2.2. Dynamic behaviour

If the potential of the electrode is perturbed by a small-amplitude sine wave potential ($\Delta E \exp(j\omega t)$) a corresponding faradaic current is obtained. Expansion of Equation 4 up to the first order leads to

$$\Delta I_F = G \Delta E + FA (k_f \Delta C_P - k_b \Delta C_Q) \quad (14)$$

where

$$G = FA (b_f k_f C_P + b_b k_b C_Q) \quad (15)$$

The perturbation induces a concentration change, ΔC_i , which is governed by

$$\frac{\partial \Delta C_i}{\partial t} = D_E \frac{\partial^2 \Delta C_i}{\partial x^2} \quad (16)$$

where i stands either for P or Q. The general solution for Equation 16 is:

$$\Delta C_i(x) = M_i \exp x (j\omega/D_E)^{\frac{1}{2}} + N_i \exp [-x(j\omega/D_E)^{\frac{1}{2}}] \quad (17)$$

if $\Delta C_i(x, t) = \Delta C_i(x) \exp j\omega t$. Hence

$$\frac{\partial \Delta C_i(x)}{\partial x} = M_i (j\omega/D_E)^{\frac{1}{2}} \exp x (j\omega/D_E)^{\frac{1}{2}} - N_i (j\omega/D_E)^{\frac{1}{2}} \exp [-x(j\omega/D_E)^{\frac{1}{2}}] \quad (18)$$

By using the same argument as in Equation 8.

$$\left. \frac{\partial \Delta C_i}{\partial x} \right|_{\phi} = 0 \quad (19)$$

From Equations 17 and 18 it follows that

$$\frac{M_i}{N_i} = \exp [-2\phi(j\omega/D_E)^{\frac{1}{2}}] \quad (20)$$

and from Equations 16 and 20

$$\Delta C_i(x) = 2N_i \exp [-\phi(j\omega/D_E)^{\frac{1}{2}}] \cosh (x - \phi) (j\omega/D_E)^{\frac{1}{2}} \quad (21)$$

Differentiating with respect to x at $x = 0$ leads to the current change, ΔI_F , through

$$\Delta I_F = FAD_E \left. \frac{\partial \Delta C_P}{\partial x} \right|_0 \quad (22)$$

and

$$\Delta I_F = -FAD_E \left. \frac{\partial \Delta C_Q}{\partial x} \right|_0 \quad (23)$$

$$\Delta I_F = -2FAD_E N_P (j\omega/D_E)^{\frac{1}{2}} \exp [-\phi(j\omega/D_E)^{\frac{1}{2}}] \sinh \phi (j\omega/D_E)^{\frac{1}{2}} \quad (24)$$

and

$$\Delta I_F = FAD_E N_Q (j\omega/D_E)^{\frac{1}{2}} \exp [-\phi(j\omega/D_E)^{\frac{1}{2}}] \sinh \phi (j\omega/D_E)^{\frac{1}{2}} \quad (25)$$

Hence

$$\frac{\Delta C_P(0)}{\Delta I_F} = -\frac{1}{FAD_E} \frac{\coth \phi (j\omega/D_E)^{\frac{1}{2}}}{(j\omega/D_E)^{\frac{1}{2}}} \quad (26)$$

and

$$\frac{\Delta C_Q(0)}{\Delta I_F} = \frac{1}{FAD_E} \frac{\coth \phi (j\omega/D_E)^{\frac{1}{2}}}{(j\omega/D_E)^{\frac{1}{2}}} \quad (27)$$

As from Equation 14

$$\Delta I_F = G\Delta E - \left[\frac{\coth \phi (j\omega/D_E)^{\frac{1}{2}} (k_f + k_b)}{(j\omega/D_E)^{\frac{1}{2}} D_E} \right] \Delta I_F \quad (28)$$

the faradaic impedance, Z_F , is equal to

$$Z_F(\omega) = R_t \left[1 + \frac{k_f + k_b}{(j\omega D_E)^{\frac{1}{2}}} \coth \phi (j\omega/D_E)^{\frac{1}{2}} \right] \quad (29)$$

where $R_t = 1/G$ is the charge transfer resistance.

2.3. Impedance for the high frequency limit

For $y \rightarrow \infty$, $\coth y \rightarrow 1$. Hence, when $\omega \rightarrow \infty$

$$\lim_{\omega \rightarrow \infty} Z_F \sim R_t \left[1 + \frac{k_f + k_b}{(j\omega D_E)^{\frac{1}{2}}} \right] \quad (30)$$

which leads to a Warburg-like behaviour in the higher frequency range.

2.4. Impedance for the low frequency limit

When $y \rightarrow 0$

$$\sinh y \sim y + \frac{y^3}{6} + \frac{y^5}{120}$$

$$\cosh y \sim 1 + \frac{y^2}{2} + \frac{y^4}{24}$$

$$\coth y \sim \frac{1}{y} + \frac{y}{3}$$

Hence when $\omega \rightarrow 0$

$$Z_F(\omega) \sim R_t \left\{ 1 + \frac{k_f + k_b}{(j\omega D_E)^{\frac{1}{2}}} \left[\frac{1}{\phi(j\omega/D_E)^{\frac{1}{2}}} + \frac{\phi(j\omega/D_E)^{\frac{3}{2}}}{3} \right] \right\} \quad (31)$$

$$Z_F(\omega) \sim R_t \left[1 + \frac{\phi}{3D_E} (k_f + k_b) + \frac{k_f + k_b}{j\omega\phi} \right] \quad (32)$$

This is the impedance of a series resistance–capacity circuit such as

$$R_p = R_t \left[1 + \frac{\phi}{3D_E} (k_f + k_b) \right] \quad (33)$$

$$C_{if} = \frac{\phi}{R_t(k_f + k_b)} \quad (34)$$

This low frequency capacity, C_{if} , is related to the total amount of redox couple on the electrode or to the surface concentration, Γ_0 (mol cm⁻²). From Equations 5, 6 and 13:

$$\frac{dC_Q}{dE} = (b_f + b_b) \left[\frac{k_f k_b}{(k_f + k_b)^2} \right] C^* \quad (35)$$

If R_t is replaced by its value (Equation 15) in Equation 34, one obtains

$$C_{if} = FA (b_f + b_b) \left[\frac{k_f k_b}{(k_f + k_b)^2} \right] \phi C^* \quad (36)$$

hence

$$\frac{dC_Q}{dE} = \frac{1}{FA} \left(\frac{C_{if}}{\phi} \right) \quad (37)$$

Integrating dC_Q/dE over the whole potential range leads to C^* , the total concentration of redox centres,

$$C^* = \frac{1}{FA\phi} \int_{-\infty}^{+\infty} C_{if} dE \quad (38)$$

which is related to the surface concentration, Γ_0 ,

$$\Gamma_0 = C^* \phi \quad (39)$$

$$\Gamma_0 = \frac{1}{FA} \int_{-\infty}^{+\infty} C_{ir} dE \quad (40)$$

2.5. Interface impedance

In addition to the faradaic impedance a parallel capacity, C , has to be taken into account. In the high frequency range the faradaic impedance is given by Equation 30 which can be rewritten in the form

$$Z_F(\omega) \sim R_t \left[1 + \frac{\mu}{(j\omega)^{\frac{1}{2}}} \right] \quad (41)$$

where

$$\mu = \frac{k_f + k_b}{(D_E)^{\frac{1}{2}}}$$

Since the Warburg-like impedance is connected in parallel to the capacity, C , the overall impedance at high frequency is given by

$$Z(\omega) = \frac{1}{\frac{1}{R_t [1 + \mu/(j\omega)^{\frac{1}{2}}]} + jC\omega} \quad (42)$$

$$= \frac{1}{\frac{(j\omega)^{\frac{1}{2}}}{R_t \mu [1 + (j\omega)^{\frac{1}{2}}/\mu]} + jC\omega} \quad (43)$$

For low values of ω ,

$$Z(\omega) \sim \frac{1}{\frac{(j\omega)^{\frac{1}{2}}}{R_t \mu} \left[1 - \frac{(j\omega)^{\frac{1}{2}}}{\mu} \right] + jC\omega} \quad (44)$$

$$\sim \frac{R_t \mu}{(j\omega)^{\frac{1}{2}} \left[1 - \frac{(j\omega)^{\frac{1}{2}}}{\mu} + R_t \mu C (j\omega)^{\frac{1}{2}} \right]} \quad (45)$$

$$\sim R_t \mu \left[\frac{1}{(j\omega)^{\frac{1}{2}}} + \frac{1}{\mu} - R_t \mu C \right] \quad (46)$$

Hence the real and imaginary parts of the impedance are:

$$Re(Z) \sim R_t \left[1 + \frac{\mu}{(2\omega)^{\frac{1}{2}}} \right] - R_t^2 \mu^2 C \quad (47)$$

$$I_m(Z) \sim \frac{R_t \mu}{(2\omega)^{\frac{1}{2}}} \quad (48)$$

The simulated impedance diagram is given in Fig. 2, together with an indication of the various parameters in the insert. It is noticeable that the diagrams are reducible in the sense that there is no change if ϕ and D are simultaneously varied while keeping the characteristic transport time ϕ^2/D_E

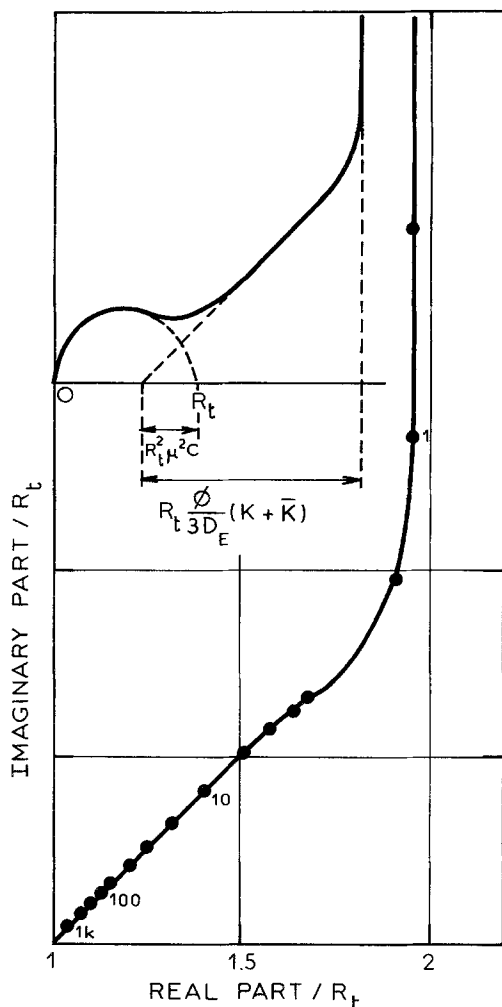


Fig. 2. Simulated faradaic impedance $Z_F(\omega)$ given by Equation 29 for $K = 3.75 \times 10^{-4} \text{ cm s}^{-1}$; $\bar{K} = 3.75 \times 10^{-4} \text{ cm s}^{-1}$; $D_E = 0.25 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$; $\phi = 10^{-4} \text{ cm}$. The insert shows a scheme of the interface impedance taking into account the parallel capacity, C .

constant. Hence the general shape of the diagram, like in all diffusion processes, is determined by the characteristic transport time, ϕ^2/D_E , without any possibility of separating these two values.

3. Experimental details

Glassy carbon disc electrodes (diameter 3 mm) were coated with $[\text{Ru}(\text{bpy})_2[\text{poly}(4\text{'-vinylpyridine)-Cl}]\text{Cl}]$ by a spin-coating technique using a methanolic solution (1 mg ml^{-1}) of the redox polymer*. Using a microsyringe, about $1 \mu\text{l}$ of this solution was placed at the surface of the glassy carbon electrode. The electrode was then spun immediately after deposition, maintaining the disc in an upward position. The procedure was repeated until a coverage of $\Gamma_0 = 2 \times 10^{-8} \text{ mol cm}^{-2}$ was attained. Measurement of Γ_0 was achieved by integrating the anodic or cathodic wave of a linear sweep voltammogram.

The impedance measurements were performed at various potentials using redox polymer-coated glassy carbon electrodes in 1 M HCl. A transfer function analyser (Solartron 1250) was used in conjunction with a potentiostat (Solartron 1186). The results are displayed in Fig. 3. The low

* $[\text{Ru}(\text{bpy})_2(\text{PVP})\text{Cl}]\text{Cl}$ polymer was kindly offered by Dr J. G. Vos and was prepared according to the procedure described in [9].

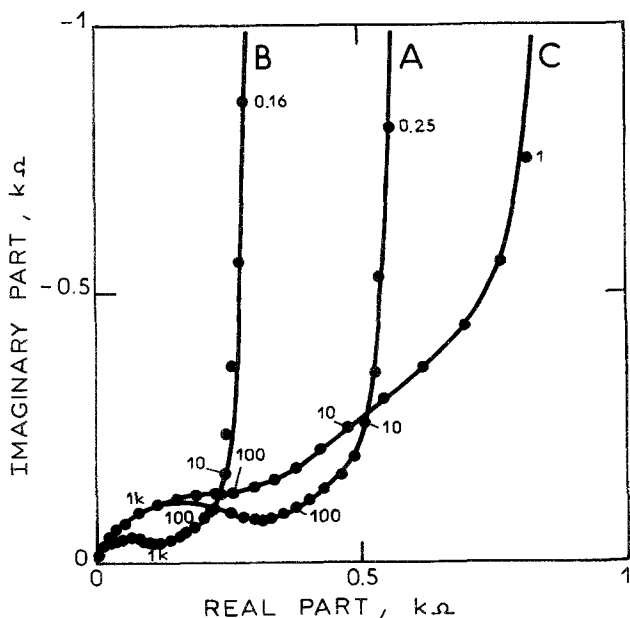


Fig. 3. Impedance measured on a GC disc electrode (3 mm in diameter) coated by $[\text{Ru}(\text{bpy})_2\text{-poly}(4'\text{-vinylpyridine})\text{Cl}] \text{Cl}$ at potentials (A) 0.64 V versus SCE; (B) 0.70 V versus SCE; (C) 0.76 V versus SCE. $\Gamma = 1.9 \times 10^{-8} \text{ mol cm}^{-2}$.

frequency capacity, C_{lf} , has been determined by considering the low frequency equivalent resistance-capacity circuit. The variation of C_{lf} is plotted versus the potential (Fig. 4). The integration of this graph leads to a value of $\Gamma_0 = 1.9 \times 10^{-8} \text{ mol cm}^{-2}$, which is very close to the value obtained by cyclic voltammetry.

4. Discussion

The simple model given in this paper is in good agreement with the experimental data obtained for the redox polymer-modified electrode. It should be noted that similar models have been used to explain more or less alike impedance curves of ion and electron insertion into a host lattice [10], injection of metal atoms into transition metal oxides for display devices [11–13], and diffusion and trapping of an electroactive species [14], but in general they are more complicated at least in the form if not in the substance.

The impedance analysis of a polymer-coated electrode should allow all the accessible parameters to be evaluated by using only one technique. Hence, this approach is very attractive for investigating modified electrodes. Experimental parameter evaluations will be reported in a subsequent paper [15].

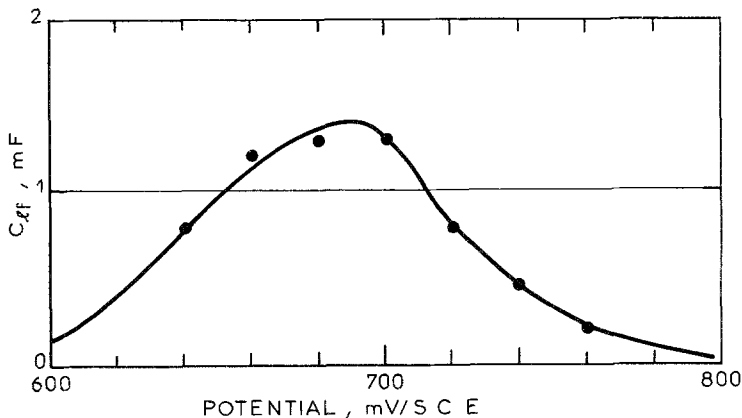


Fig. 4. Variation of the low frequency capacity, C_{lf} , versus the potential. Electrode diameter, 3mm.

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