Transport across an electroactive polymer film in contact with media allowing both ionic and electronic interfacial exchange

M.A. Vorotyntseva,*, C. Deslouisb, M.M. Musianic, B. Tribolletb, K. Aoki

aDepartment of Applied Physics, Fukui University, 3-9-1 Bunkyo, Fukui-shi 910, Japan
bUPR 15 CNRS Physique des Liquides et Electrochimie, 4 pl. Jussieu, 75252 Paris Cedex 05, France
cIPELP CNR, 4 Corso Stati Uniti, 35127 Padova, Italy

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Abstract

In this paper, the general theory of coupled electron-ion transport inside a film having a mixed electron-ion conductivity is applied, and the a.c. impedance expressions have been calculated for the situations where the film can exchange electrons and/or ions with the surrounding media. Important example of such system is given by a conducting polymer film between two solutions containing a redox active couple ("redox active solutions") which is subjected to a faradaic process at the film surface with the participation of electronic species inside the film. As particular cases, the general formula describes also the systems where one or both interfacial boundaries can only be crossed by one type of charged species, electrons or ions. Besides the previously analysed situations, metal/film/metal, metal/film/background solution, or a film between two background solutions, we have obtained expressions for impedance of the film between a redox active solution and a background (without redox species) one, or between a metal and a redox active solution. Theoretical predictions for the shapes of complex impedance plots in the case of a redox active solution have been demonstrated. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Complex impedance is one of the major techniques for experimental study of electroactive polymer films. The possibility to vary the perturbing frequency within a very wide interval enables it to provide characteristics of numerous bulk film and interfacial processes in those systems. However, the overlap of the frequency domains where each of these processes plays a significant role in the overall signal leads to the necessity of an adequate theoretical interpretation to unravel their respective contributions.

During an extended period, this method was applied to the simplest examples of "symmetrical" and "asymmetrical" systems (according to Buck [1, 2]) of this kind, a film between two metals [3] or two identical solutions [4], or metal/film/solution [5, 6]. In those cases the solution only contains ions which do not possess a redox activity ("background electrolyte"). The counter-ion is able to cross the film/solution boundary to retain the bulk film electroneutrality. Thus, in all the above systems there is only one charged species, electron or anion (the counter-ion involved for unsubstituted polymer films which become conductive upon oxidation), which can pass the current through each particular interface. Recent results in this direction, in
particular with account of the Poisson equation instead of the local electroneutrality condition, may be found in references [7–9], see also references in [6, 10].

These three simpler systems have been recently analysed on the basis of the general theory of coupled electron-ion transport which generalises the Nernst–Planck equations [11]. The relevant impedance expressions were obtained as follows (denotations below correspond to those in reference [11]):

\[
Z_{m/f/m}(\omega) = R_m^{\infty} + R_t + R_f^{\infty} + 4\eta_m^2 \Delta R z_{th}\]
\[
z_{th}(v) = v^{-1} \tanh v \tag{1}
\]

\[
R_t = L_k^{-1}, \quad \Delta R_t = L \left( 4DC \right)^{-1},
\]
\[
v = \left( \frac{k_0L^2}{4D} \right)^{1/2} \tag{2}
\]

redox inactive solution/film/redox inactive solution (s/f/s) [4]:

\[
Z_{s/f/s}(\omega) = R_s + R_s^{\infty} + R_t + R_f^{\infty} + R_t^{\infty} + R_{s2} + 4\eta_s^2 \Delta R z_{th} \tag{3}
\]

metal/film/redox inactive solution (m/f/s) [5, 6]:

\[
Z_{m/f/s}(\omega) = R_m^{\infty} + R_t + R_f^{\infty} + R_s + \Delta R_t
\]
\[
\left[ z_{th} + (t_e - t_i)z_{th} \right], \quad z_{th}(v) = v^{-1} \coth v \tag{4}
\]

Those formulae contain: frequency, \( \omega \), film thickness, \( L \), redox capacitance (quasi-equilibrium) per a unit volume of the film, Eq. (10), \( C_{\rho} \), three macroscopic transport parameters of the polymer phase: \( D \), binary diffusion coefficient, \( t_e = 1 - t_o \), (migration) transference numbers of electrons and ions, \( \kappa \), specific electron-ion conductivity, as well as resistances of the interfacial exchange with the corresponding charged species, electron for the metal/film boundary (\( R_m^{\infty}, R_f^{\infty} \)), or ion for the inactive solution/film one (\( R_s^{\infty}, R_f^{\infty} \)) and the ohmic resistances of the solutions in contact, depending on the systems (\( R_{s1}, R_{s2}, R_t \)).

One should keep in mind that capacitance terms due to the interfacial charging (“double-layer effects”) are disregarded in this derivation. As a consequence, all interfacial and bulk-solution contributions in Eqs. (1)–(4) are simply added in those systems to the bulk-film ones. Expressions of those macroscopic transport parameters via microscopic “friction coefficients” are given in [11].

Important additional information concerning the properties of the film may be obtained by measurements in presence of a redox active couple inside the solution(s) in contact. Such experimental studies have already been carried out for two geometries of the system, metal/film/redox active solution (m/f/es) [12–14] and a film between two redox active solutions (es/f/es) [15]. The interpretation of those data requires the corresponding generalisation of the theory. It has been carried out in this paper within the framework of the assumption that the solution contains an excess of the “background” electrolyte (as earlier, it means no redox activity while its anion is able to cross the interfacial boundary). Redox active species are supposed to be only present in the solution phase but not inside the film, and they participate in the interfacial electron exchange with the polymer at the film/solution boundary. One can expect such a behaviour if the redox species have a sufficiently large size and/or they are repelled by the space-charge region at the film/solution interface as for a permselective membrane.

The analysis developed in this paper is based on the same concepts as those used in [11]. However, the existence of both electron and ion interfacial fluxes at the film/solution boundaries (such interfaces are referred below as “es”) leads to an essential modification of the boundary conditions for those transport equations. Their solution has enabled us to obtain a general analytical expression for the complex impedance of the system, which can correspond to different types of interfaces and contains, in a complicated manner, bulk parameters of all three phases as well as characteristics of the interfacial electron and ion transfer.

No symmetry of the system has been assumed in the course of its derivation so that the solutions in contact may have quite different compositions. The only restriction is an assumption of no concentration gradients in the unperturbed state, i.e. no direct current at zero amplitude of the perturbation.

The latter requirement specifies possible types of the system:

- **es/f/es**: symmetrical case (identical redox active solutions) with a zero bias voltage between the bulk solutions,
- **s/f/es**: background solution/film/redox active solution. It corresponds to an infinite value of the interfacial impedance of the electronic exchange. The bias voltage must be adjusted to realise a zero background anion flux across the system,
- **m/f/es**: metal/film/redox active solution. Surprisingly, the result for this case can be immediately obtained from the general formula if the interfacial resistance of ionic transfer is infinitely large while the bulk ohmic resistance of this medium is very small. In this last situation, the bias voltage must deliver a zero value of the electronic flux.
2. Transport relations and boundary conditions

Adequate description of transport phenomena in electroactive polymer films means to take into account numerous factors like a disordered type of the polymer phase, high concentrations of electronic and ionic species, their short-range interactions, inhomogeneity effects, “hopping” type of the electronic motion in certain systems (e.g. interchain transport in conducting polymers), coupling between the electronic and ionic fluxes, etc. Thus, application of the traditional set of Nernst–Planck–Einstein transport relations should be used as a simple approximation to elucidate the situation.

Essentially more substantiated approach is based on the formulae of the “multi-component diffusion” [16] relating the gradients of electrochemical potentials of the components with the fluxes. It has been shown in [11] for the case of any small-amplitude perturbation that those relations for the coupled transport of two species, electrons and counter-ions can be replaced by the conservation in space of the overall current density \( \hat{\mathbf{r}} \):

\[
\Delta \hat{\mathbf{r}} = 0
\]

and by the usual non-stationary diffusion equation for several other characteristics of the system:

\[
\partial \Phi / \partial t = D \nabla^2 \hat{\mathbf{r}}, \quad \partial \Phi_{ei} / \partial t = D \nabla^2 \Phi_{ei}, \quad \partial \rho / \partial t = D \nabla^2 \rho
\]

Here, \( i \) and \( i' \) are related to the partial current densities of electrons \( \hat{\mathbf{r}} \) and ions \( \hat{\mathbf{r}}_e \),

\[
i_{\text{e,i}} = i_{\text{e,i}} + i_i \\
i'_{\text{e,i}} = i_{\text{e,i}} - i_i
\]

\( \Phi_{ei} \) is a combination of the perturbed parts of the electrochemical potentials of electrons and ions (an analogue of the chemical potential of the salt in the theory of solutions but in units of potential rather than those of energy):

\[
\Phi_{ei} = \mu_{\text{e,i}} F - \mu_{\text{e,i}}^0 F
\]

where \( F \) is the Faraday number, \( \rho \) is equal to the local electronic charge, \( \rho_e \), and (with minus sign) to the ionic one:

\[
\rho \equiv \rho_e = -\rho_i
\]

Macroscopic transport parameters, \( D, \ i_{\text{e,i}}, \ \kappa \), have been introduced in Section 1.

The above local characteristics of the film are related by equations

\[
\hat{\mathbf{r}} = -D \nabla \rho, \quad \partial \rho / \partial t = -\nabla \hat{\mathbf{r}}, \quad \rho = C_{\Phi} \Phi_{ei}
\]

In the case of a one-dimensional system and a low-amplitude sinusoidal perturbation, the complex amplitude of the overall current density is a constant, and Eqs. (6) and (10) give:

\[
d^2 \hat{\mathbf{r}} / dx^2 = j_0 \omega \hat{\mathbf{r}}
\]

\[
\Phi_{ei} = -j_0 C_{\Phi} \partial \hat{\mathbf{r}} / dx
\]

Another important formula relates the differences between the values of the electrochemical potentials at two film boundaries with the variation of \( \Phi_{ei} \):
“indifferent” one since its anion may cross the interface and play the role of a counter-ion for the electronic charge compensation inside the film.

Within the linear response approximation with respect to the amplitude of the perturbation, this process of ionic interfacial exchange is considered here in a simplified way by assuming that the interfacial ionic exchange impedance is a resistance, $R_s^{\text{es}f}$, in other words that the difference of the corresponding electrochemical potentials is proportional to the partial ionic current across the interface with a real factor:

$$\left[ \mu_i^e(0) - \mu_i^f(0) \right] (z_iF)^{-1} = R_s^{\text{es}f} i(0)$$

(14)

As the redox species cannot penetrate the film (starting hypothesis), the boundary condition for the electronic charge carriers at the redox active solution/film interface (es/f), $x = 0$, has a similar form:

$$\left[ \mu_i^e(0) - \mu_i^f(0) \right] (z_iF)^{-1} = R_s^{\text{es}f} i(0)$$

(15)

where, $R_s^{\text{es}f}$ is the interfacial electron transfer resistance. The electronic electrochemical potential, $\mu_e^f$, is defined as the difference between the electrochemical potentials of the redox couple components. Their variation within the Nerst layer of the solution due to the concentration polarisation of redox species is also proportional to the partial electronic current so that:

$$\left[ \mu_i^e(-\delta) - \mu_i^f(0) \right] (z_iF)^{-1} = W_s i(0)$$

(16)

In the case of a molecular diffusion transport of redox species, the second contribution in Eq. (16) is given by the Warburg impedance. More generally, it corresponds to a convective diffusion impedance (see further). In both cases, migration contribution is negligible in the presence of a background electrolyte.

As a result, the overall difference of the electronic electrochemical potential in those regions is determined by the total electronic impedance of the interfacial and diffusional processes:

$$\left[ \mu_i^e(-\delta) - \mu_i^f(0) \right] (z_iF)^{-1} = Z_s^{\text{es}f} i(0)$$

(17)

$$Z_s^{\text{es}f} = R_s^{\text{es}f} + W_s$$

(18)

At this stage, one could envision a more complicated interfacial processes for the Faradaic path (involving, for example, an adsorption–desorption step for the redox species at the film in quasi-equilibrium conditions) which would simply need to replace the interfacial resistance, $R_s^{\text{es}f}$, by a Faradaic impedance $Z_s^{\text{es}f}$.

In the bulk solution, the change of both electrochemical potentials is determined by their electric component (Galvani potential) which is proportional to the overall current density:

$$\left[ \mu_i^e(-\infty) - \mu_i^f(0) \right] (z_iF)^{-1} = \left[ \mu_i^e(-\infty) - \mu_i^f(-\delta) \right] (z_iF)^{-1} = R_s^\text{ed} i$$

(19)

where $R_s^\text{ed}$, ohmic resistance of the electrolyte solution. As usual, the variations of the electric potential and correspondingly of the ionic electrochemical potential within the Nerst layer will be neglected.

At the reference electrode in solution 1 ($x < 0$), the amplitudes of individual electrochemical potential variations are immediately related to those of the electrode potential $E$:

$$\mu_i^e(-\infty)(z_iF)^{-1} = \mu_i^e(-\infty)(z_iF)^{-1} = E.$$  

(20)

Then, one can derive a boundary condition for the currents inside the film near this interface, with the use of Eqs. (12) and (8).

$$\left( \sum \omega C \right)^{-1} \frac{d^j}{dx} = R_s^{\text{es}f} i(0) - Z_s^{\text{es}f} i(0), \quad x = 0$$

which can be transformed by means of relations (7):

$$\left( \sum \omega C \right)^{-1} \frac{d^j}{dx} = i \left( \sum \omega C \right)^{-1} \left( R_s^{\text{es}f} + Z_s^{\text{es}f} \right), \quad x = 0.$$  

(21)

If the potential of bulk solution 2 ($x > \delta$) is taken as a reference value, the variations of both electrochemical potentials in that region ($x \rightarrow + \infty$) equal zero, instead of Eq. (20) so that

$$\mu_i^e(L + \delta)(z_iF)^{-1} = \mu_i^f(L + \delta)(z_iF)^{-1} = R_s^\text{ed} i.$$  

(22)

Analogue of Eqs. (14) and (17) at another boundary, film/redox active electrolyte (f/es), has the form:

$$\left[ \mu_i^e(L) - \mu_i^f(L + \delta) \right] (z_iF)^{-1} = Z_s^{\text{es}f} i(L),$$  

(23)

$$\left[ \mu_i^e(L) - \mu_i^f(L + \delta) \right] (z_iF)^{-1} = R_s^{\text{es}f} i(L).$$  

(24)

One can combine them again to obtain another boundary condition for the currents, compare Eq. (21):

$$\left( \sum \omega C \right)^{-1} \frac{d^j}{dx} = i \left( \sum \omega C \right)^{-1} \left( R_s^{\text{es}f} + Z_s^{\text{es}f} \right), \quad x = L.$$  

(25)

Electronic impedance in these relations is given by a formula similar to Eq. (18):

$$Z_s^{\text{es}f} = R_s^{\text{es}f} + W_s.$$  

(26)
Generally, there is an asymmetry of interfacial and/or anion transport inside the polymer film, and it is interesting to note that another interfacial boundary, metal/film, can also be treated as a particular case of the above formulae after replacing:

\[ R_i^{\text{eff}} \rightarrow \infty, \quad Z_\text{eff}^i \approx R_i^{\text{eff}} i_0(0) = 0, \quad i(0) = i. \]  

(29)

4. Current distribution and impedance

General solution of Eq. (11) may be written as:

\[ \tilde{i}(x) = \left[ \tilde{i}(L) \sinh 2vx/L + \tilde{i}(0) \sinh 2v(1 - x/L) \right] / \sinh 2v \]  

(30)

so that

\[ \Phi_{\text{el}}(x) = -\int \left( \tilde{i}(L) \sinh 2vx/L + \tilde{i}(0) \cosh 2v(1 - x/L) \right) / \sinh 2v \]  

(31)

where, \( W_f \) is the Warburg impedance for the electron-anion transport inside the polymer film,

\[ W_f = W_f(v) = (\mu_0 L \varepsilon_0)^{-1} = A R_f, \quad v \text{ and } A R_f, \quad \text{see Eq.(2).} \]  

(32)

Then, one should insert expression (31) into conditions (21) and (25) to get a set of two linear equations for \( i(0) \) and \( i(L) \). Their solution may be written as:

\[ i(0) = i(0) = i(L) = i, \quad Z_\text{eff}^i = Z_\text{eff}^i \]  

(27)

The above relations include an inactive electrolyte solution in the particular case of a very large value of the interfacial charge-transfer resistance in Eq. (18) resulting in Eq. (28) for s/f:

\[ i(0) = 0, \quad i(0) = i. \]  

(28)

For a symmetrical system, s/f/s, es/f/es or m/f/m, Eq. (27), these expressions are strongly simplified:

\[ \tilde{i}(L) = \tilde{i}(L) = \tilde{i}(L) = \tilde{i}(L) \]  

(34)

To derive an expression for complex impedance for the general case of a non-symmetrical system, one should combine Eqs. (20), (17), (13), (23) and (22) to obtain:

\[ Z_{\text{es/f/es}} = \frac{Z_{\text{es/f/es}}}{Z_{\text{es/f/es}} + Z_{\text{es/f/es}}} \]  

(35)

\[ i(0) = i(0) = i(0) = i(0) \]  

(36)

(37)

Then, the expressions for \( i_0 \) and \( \Phi_{\text{el}} \) should be taken from Eqs. (30) and (31), with the use of Eqs. (33) and (34). The final formula can be represented in the form:

\[ Z_{\text{es/f/es}} = Z_{\text{es/f/es}} + Z_{\text{es/f/es}} + Z_{\text{es/f/es}} \]  

(38)

\[ Z_{\text{es/f/es}} = Z_{\text{es/f/es}} + Z_{\text{es/f/es}} \]  

(39)

There are numerous particular cases where this formula may be markedly simplified.

Symmetrical membrane geometry with redox active electrolyte: es/f/es, with conditions (27) fulfilled. Then,
Frequency dependence of the impedance in the above formulae appears from the hyperbolic functions as well as from the "diffusion impedances" inside the film, \( W_f \) [Eq. (32)], and of the redox couple in solution, \( W_s \) [Eqs. (18) and (26)]. Simple interpolation approximation will be used below for the latter quantity:

\[
W_s = \sigma j_0 \frac{1}{2} \tanh \left( \frac{j_0}{\sigma} W_s \right)^{-1}
\]

which reproduces both the Warburg behaviour with a constant, \( \sigma \), at sufficiently high frequencies and the stationary diffusion across the Nernst layer, \( W_s^\infty \). Here,

\[
\sigma = RT(nF)^{-1} [c_{ox}(D_{ox})^{-1/2} + c_{red}(D_{red})^{-1/2}]
\]

where \( c_{ox} \) (\( c_{red} \)) bulk concentration of the Ox (Red) form, \( D_{ox} \) (\( D_{red} \)), their diffusion coefficients inside the solution, \( \delta \), Nernst layer thickness.

\( W_s \) is more adequately described as a convective diffusion impedance when there is an imposed convection in the bulk solution. For example, an accurate expression has been proposed in the case of a rotating disk electrode, \( W_s = R_d(1/\theta_s)^3 \), where \( R_d = W_s^\infty \) is the diffusion resistance and \((1/\theta_s)^3\) is a function of frequency varying between 0 and 1 which has been tabulated in [17].

Resistances of the interfacial electron exchange, \( R_s^\infty \), \( R_f^\infty \), depend also on the concentrations of Ox and Red species in the solution. To avoid a detailed specification of its mechanism, the case of equal concentrations, \( c_{ox} = c_{red} \), is considered below and the resistance for the symmetrical system, es/f/es, is assumed to be inverse proportional to this concentration:

\[
R_s^\infty = \frac{RT}{nF^2 k_c c_{ox}}
\]

As it has been established in the previous paper [11] the bulk film transport can be adequately characterised by 4 macroscopic parameters (dependent on the film charging level), high-frequency resistance \( \kappa \), transference numbers of electrons and ions \( t_e = 1-t_i \), binary diffusion coefficient \( D \) and redox capacitance \( C_{pr} \) see Section 1. Individual diffusion coefficients of electronic species and ions, \( D_e \) and \( D_i \), do not appear in these theoretical equations. However, one can introduce those characteristics in a manner similar to the diluted electrolyte solutions, by postulating relations (52) as the definition of \( D_e \) and \( D_i \):

\[
t_{e,i} = \frac{D_{e,i}(D_e + D_i)^{-1}}{2D_e D_i(D_e + D_i)^{-1}}\]

\[\text{Section 1. Individual diffusion coefficients of electronic species and ions, } D_e \text{ and } D_i \text{, do not appear in these theoretical equations. However, one can introduce those characteristics in a manner similar to the diluted electrolyte solutions, by postulating relations (52) as the definition of } D_e \text{ and } D_i:\]

\[t_{e,i} = \frac{D_{e,i}(D_e + D_i)^{-1}}{2D_e D_i(D_e + D_i)^{-1}}\]
\[ D_e = D(2t_0)^{-1}, \quad D_i = D(2t_0)^{-1} \]  

One should keep in mind that those parameters do not correspond in a general case to the proportionality coefficients between the partial currents of electrons and ions, \( i_e \) and \( i_i \), and the gradients of their concentrations, or their chemical potentials. The latter depend essentially on the way to introduce a non-thermodynamic quantity, Galvani potential \( \phi \). The above correspondence can only be reached if the Galvani potential is defined in a quite certain way dependent on the transport properties of the medium [18].

5. Discussion

In view of the complexity of the equations describing the impedance of the system in the different possible geometries, their analysis does not allow to appreciate all relevant features. Therefore, a set of theoretical impedance diagrams was calculated, in order to establish the effect of various physical parameters. The diagrams presented hereafter correspond to several combinations of the rates of the current/transport processes, i.e. redox exchange at the f/es interface(s), the mass transfer in solution and ion transport across the film and at its interface(s). Electron transport in the film was always assumed to be fast. The following discussion is focused on the es/f/es and the m/f/es systems for which previous experimental work has been performed [12–15]. The former has been considered in the symmetrical case only.

In those simulations the number of transferred electrons was put equal to 1, diffusion coefficients of Ox and Red species, \( D_{ox} = D_{red} = 10^{-5} \text{ cm}^2 \text{ s}^{-1} \). Values of reaction constant \( k_e \) and concentrations \( c_{ox} = c_{red} \) are indicated for each plot.

Zero solution resistance was assumed. No contribution by interfacial capacitance was considered. Therefore, actual diagrams would differ from the calculated ones for the presence of an additional HF loop.

5.1. Membrane between two redox active electrolytes: es/f/es

Fig. 1 shows theoretical impedance diagrams for a membrane in contact with two identical solutions with which electrons are easily exchanged (fast redox system), while both the ion transport inside the film and the ionic interfacial exchange are slow (large \( D_i \)). The curves correspond to three different mass transfer rates. Under these conditions the behaviour of the system is dominated by the “electronic path”: the HF limit of the impedance is the sum of two identical \( R_0^{\text{es/f}} \) terms (one for each interface), the pseudo-diameter of the loop is proportional to \( \delta \) and its characteristic frequency is controlled by \( D_e \). At LF the shape of the diagrams differs from that typical of a convective diffusion impedance owing to the relaxation associated with ion transport. These diagrams are similar to those experimentally obtained for polypyrrole membranes in contact with ferricyanide/ferrocyanide solutions (see Fig. 6 in reference [14]), a system which had been chosen as the model of a fast redox couple reacting on the membrane with a low ionic conductivity.

Figure 2 shows the effect of the ionic interfacial resistance, \( R_0^{\text{s/f}} \), other conditions being essentially the same as for Fig. 1. As \( R_0^{\text{s/f}} \) becomes comparable to \( R_0^{\text{es/f}} \), the HF limit of impedance shifts to a lower value, corresponding to the parallel combination of both resistances. This result shows that membranes having the same rate of electron exchange with a redox species but various rates of ion exchange would give diagrams with different HF impedance limits (i.e. with HF loops of different sizes if capacitances were considered). Therefore, erroneous conclusions on the electrocatalytic activity of different polymers could be drawn if the HF loops were ascribed to electron transfer only. On the other hand, the same figure shows that the LF limit of the impedance is independent of \( R_0^{\text{s/f}} \) which means that, owing to the low \( D_i \) value, the “ionic path” is still negligible in d.c.

Fig. 3 shows the effect of increasing the ion diffusion coefficient inside the film, \( D_i \), other conditions being the same as in Fig. 2 (with a large \( R_0^{\text{es/f}} \) value). As the ion mobility becomes larger, the relative importance of the ionic path increases and the LF limit of the impedance is reduced, even if \( R_0^{\text{es/f}} \ll R_0^{\text{s/f}} \). At the same time, the relaxation associated to ion transport in the film shifts to a higher frequency range, so that the loops no longer look flattened at LF. Of course, if one deals with the membrane with a low value of interfacial ionic resistance \( R_0^{\text{s/f}} \) (e.g. about 5 \( \Omega \) \text{ cm}^2—diagrams not shown), the dependence on \( D_i \) is of the same type but much more pronounced.

All diagrams discussed so far have been calculated for a fast redox exchange at the f/es interface. Analogous to Fig. 2, Fig. 4 shows the effect of \( R_0^{\text{es/f}} \) but for a slower redox exchange. In this case, as \( R_0^{\text{es/f}} \) becomes smaller, the LF limit of the impedance decreases, as discussed for Fig. 2, but the LF limit is also affected because the ionic path may favourably compete with the electronic one which is slowed down by a sluggish interfacial exchange.

Other calculated diagrams showed that in the case of a slow redox system and a fairly fast ion transport, the effect of mass transfer in solution was fairly small and mainly appeared at low frequency. The effect of \( D_i \) was similar to that described for a fast redox system.
5.2. Modified electrode geometry with redox electrolyte: m/f/es

Figures 5 and 6 show the effect of mass transfer for the m/f/es geometry in two cases where the ion transfer resistance is comparable (Fig. 5), or greater (Fig. 6) than the electron exchange resistance.

The Nyquist plots in Fig. 5 look like perfect semicircles, though a Warburg domain does exist in the HF range (see below). Although the shape of these diagrams is similar to that of a parallel RC combination, their characteristic frequency shifts towards LF upon increasing the value. Fig. 5 reproduces quite well diagrams experimentally obtained on polyaniline-coated Pt rotating disc electrodes in contact with acid solutions containing either ferricyanide/ferrocyanide (see Figs. 3 and 4 in reference [12]) or Fe²⁺/³⁺ (see Figures 7 and 8 in reference [14]) couples. Well-shaped semicircles are not observed in Fig. 6 corresponding to a slow ion transport. As the modified electrode geometry is blocking for ions in the d.c. limit, the LF behaviour depends only on the electronic path. In both Figs. 5 and 6 the diameter, or pseudo-diameter, of the loop is proportional to the diffusion layer thickness.

Comparison of Figs. 1 and 6, for which the same numerical values were attributed to all parameters, shows that diagrams of a similar shape are obtained for both geometries in the case of slow transport, impedance being about twice larger for es/f/es than that for m/f/es, as $R_{m/f}$ was assumed to be small. Such a similarity does not exist when ion transport is fast (cf. Figs. 3 and 5, though parameters were not identical for these figures).

Fig. 7 shows the effect of $D_i$, again for a fast redox exchange and a low value of $R_{m/f}$. The HF limit (which depends only on the interfacial resistances) and the LF limit (which is only associated with the electronic path) are independent of $D_i$, but the shape of the diagrams

Fig. 1. Calculated impedance diagrams for the symmetrical es/f/es system, Eq. (40), and the set of parameters: $R^{es}_{f/s} = 20 \Omega$ cm² (corresponding to $k^{es} = 10^{-2}$ cm s⁻¹, $c_{ox} = c_{red} = 1.3 \times 10^{-2} M$, $n = 1$), $R^{i}_{f/s} = 500 \Omega$ cm², $\alpha = 125 \Omega$ cm² s⁻¹/² (corresponding to $D_{ox} = D_{red} = 10^{-3}$ cm² s⁻¹), $B = 6 \times 10^{-9}$ cm² s⁻¹, $t_i = 3 \times 10^{-7}$ (corresponding to $D_i = 3 \times 10^{-9}$ cm² s⁻¹, $D_e = 10^{-4}$ cm² s⁻¹), $\Delta R_i (= L (4DC_{r})^{-1}) = 4170$ Ω cm² (corresponding to film thickness $L = 1.5 \times 10^{-3}$ cm, redox capacitance $C_p = 15 F$ cm⁻³). Rate of the diffusional transport in the solution is variable: $W^{ox} = 80, 120, 160$ cm⁻² [corresponding to diffusion layer thickness $\delta = 2 \times 10^{-3}$ (△), $3 \times 10^{-3}$ (●), $4 \times 10^{-3}$ (■) cm]. (a) Nyquist plot; (b) Imaginary part vs frequency plot.

Fig. 2. See Fig. 1. $W^{ox} = 120$ Ω cm² ($\delta = 3 \times 10^{-3}$ cm). Variation of the interfacial ionic transfer resistance: $R^{i}_{f/s} = 5$ (△), $50$ (●), $500$ (■), $5000$ (■) Ω cm² for the case of a fast electron exchange at the interfaces.

Fig. 3. See Fig. 2. $R^{es}_{f/s} = 500$ Ω cm². Variation of the ionic diffusion coefficient, $D_i = 10^{-6}, 10^{-7}, 10^{-8}$ cm² s⁻¹ corresponding to $D \approx 2 D_p$, $t_i \approx D_i/D_p$. The case of a fast electron exchange at the interfaces.
changes markedly. Upon increasing $D_i$ values the loop associated to ion transport shifts to higher frequency and increases in size. For $D_i = 10^{-6}$ cm$^2$ s$^{-1}$ the diagram consists of a Warburg line in the HF domain and a seemingly capacitive loop at LF. These are the features experimentally observed on poly(N-ethylcarbazole)-coated Au rotating disc electrodes in contact with acid solutions containing the hydroquinone/benzoquinone couple (see Fig. 3 in reference 12). For $D_i = 10^{-8}$ cm$^2$ s$^{-1}$ the shape is more complicated and three time constants are detectable.

Fig. 8 shows the effect of $R_i^{es}$ for the modified electrode geometry, under the same conditions chosen for Fig. 2. Again the effect of decreasing $R_i^{es}$ is that of shifting the HF limit of the impedance to lower values. Therefore, an accurate determination of the charge transfer resistance of the faradaic process occurring at the $es/f$ interface is subject to the same limitations described for the $es/f/es$ system.

Fig. 9 shows diagrams corresponding to a slow redox exchange. The same numerical values as in Fig. 4 were attributed to all parameters. In this geometry $R_i^{es}$ affects the HF limit and the medium frequency range
of the impedance, while the LF limit is fixed by the electronic path.

In the case of a slow redox exchange the effect of $D_l$ is similar to that described by Eq. (41) for a fast exchange. The effect of diffusion layer thickness $\delta$ is very limited.

Fig. 7. Modified electrode geometry, m/f/es, Eq. (41), fast electron exchange. Variation of the ionic diffusion coefficient, $D_i = 10^{-8} \left(\Delta\right), 10^{-7} \left(\bullet\right), 10^{-6} \left(\Box\right) \text{cm}^2 \text{s}^{-1}, R_m^\text{f/s} = 5 \text{ cm}^2, R_{m/f}^\text{f/s} = 5 \text{ cm}^2$. Values of other parameters are identical to those in Fig. 3. (a) Nyquist plot; (b) Imaginary part vs frequency plot.

Fig. 8. Modified electrode geometry, m/f/es, Eq. (41), fast electron exchange. See Fig. 2. $R_m = 5 \text{ cm}^2, R_{m/f} = 5 \left(\Delta\right), 50 \left(\Box\right), 500 \left(\bullet\right), 5000 \left(\ast\right) \text{ cm}^2$.

Fig. 9. Modified electrode geometry, m/f/es, Eq. (41), slow electron exchange. See Fig. 4. $R_m^\text{s/l} = 5 \text{ cm}^2$.

6. Conclusions

This paper was aimed at providing a comprehensive description of the electrochemical behaviour of a film having mixed electron-ion conduction, and liable to exchange electrons and/or ions with surrounding media. The bulk transport processes were analyzed in the framework of the theory of coupled electron-ion transport, which accounts for the specific case of concentrated media. Interfacial exchanges were considered on a thermodynamic approach using electrochemical potentials for ions and electrons.

The obtained impedance expressions address all possible situations for the media contacting the film, i.e. either a purely electronic exchange (metal), or a purely ionic exchange (solution with a background electrolyte), or a mixed exchange (solution with background electrolyte and a redox couple).

The validity range of all the results obtained here is defined by the quasi-equilibrium conditions and also by the absence of Faradaic reactions between the redox couple and the polymer moieties within the film.

Similarly to the case of the “blocked” situation, corresponding to the absence of redox species in solution, simulated diagrams show that a direct comparison between the different data for the same film but for different boundary conditions (i.e. either as a free-standing membrane or as a modified electrode and with or without redox species in both cases) is even more crucial.

It must be emphasized that a careful control of convective mass transport is required here, at variance with the s/l situation for which no concentration gradient of the background electrolyte was observed in solution. This makes it possible to extract the interfacial impedance ascribed to electronic exchange even in the limiting situation of rapid interfacial ionic transfer, of highest interest in the case of electrocatalysis and simply treated in this work as a resistance.
Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_r$</td>
<td>redox capacitance per unit volume</td>
</tr>
<tr>
<td>$D$</td>
<td>binary electron-ion diffusion coefficient</td>
</tr>
<tr>
<td>$E$</td>
<td>electrode potential</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday number</td>
</tr>
<tr>
<td>$i$</td>
<td>instantaneous current density</td>
</tr>
<tr>
<td>$i_e$, $i_i$</td>
<td>instantaneous values of partial current densities (e = electron, i = ion)</td>
</tr>
<tr>
<td>$i^*$</td>
<td>&quot;residual&quot; current density</td>
</tr>
<tr>
<td>$L$</td>
<td>film thickness</td>
</tr>
<tr>
<td>$R_f$</td>
<td>high-frequency bulk-film resistance</td>
</tr>
<tr>
<td>$R_{m/f}$, $R_{f/m}$, $R_{s/f}$, $R_{f/s}$</td>
<td>interfacial electron-transfer resistances [m = metal, f = film, s = (redox active) solution]</td>
</tr>
<tr>
<td>$R_{i/f}$, $R_{i/s}$</td>
<td>interfacial ion-transfer resistances (f = film, s = solution)</td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
</tr>
<tr>
<td>$t_e$, $t_i$</td>
<td>migration (high-frequency) bulk-film transference numbers (e = electron, i = ion)</td>
</tr>
<tr>
<td>$W_f$</td>
<td>Warburg impedance for the electron-anion transport inside the polymer film</td>
</tr>
<tr>
<td>$W_{s1}$, $W_{s2}$</td>
<td>convective diffusion impedance of redox species in the corresponding solution (Warburg impedance for the purely diffusional transport)</td>
</tr>
<tr>
<td>$x$</td>
<td>coordinate normal to both interfaces</td>
</tr>
<tr>
<td>$z_e$, $z_i$</td>
<td>charge valencies of electrons or ions</td>
</tr>
<tr>
<td>$Z_{m/e/f}$, $Z_{s/e/s}$, $Z_{m/e/e}$</td>
<td>complex impedance of the film in contact with two surrounding media (m = metal, f = film, s = redox inactive solution, es = redox active solution)</td>
</tr>
<tr>
<td>$R_{s1}$, $R_{s2}$, $R_s$</td>
<td>ohmic resistances of the bulk solution</td>
</tr>
<tr>
<td>$Z_{s/e}$, $R_{s/e}$, $Z_{s/f}$, $R_{s/f}$</td>
<td>amplitudes of the Warburg impedance inside the film ($W_f = \Delta R_f/v$ defined by Eq. (2))</td>
</tr>
<tr>
<td>$\delta$</td>
<td>diffusion layer thickness for an electroactive redox species in the Nernst approximation</td>
</tr>
<tr>
<td>$\Phi_{ai}$</td>
<td>combined electron-ion potential, Eq. (18)</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>high-frequency bulk conductivity of the film</td>
</tr>
<tr>
<td>$\mu_e$, $\mu_i$</td>
<td>perturbations of the electrochemical potentials (e = electron, i = ion)</td>
</tr>
<tr>
<td>$\mu e^{-\infty}$, $\mu i^{-\infty}$</td>
<td>perturbations of electrochemical potentials in the bulk solution phase</td>
</tr>
<tr>
<td>$\nu = \frac{(\rho_0 L^2)}{4D} V^{1/2}$</td>
<td>dimensionless function of frequency, Eq. (2)</td>
</tr>
<tr>
<td>$\rho = \rho_e$, $\rho_i$</td>
<td>perturbations of the electron and ion charge densities (e = electron, i = ion)</td>
</tr>
<tr>
<td>$\omega$</td>
<td>frequency (rad s$^{-1}$)</td>
</tr>
</tbody>
</table>

Acknowledgements

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References