

Theory of the Impedance of Electron Diffusion and Recombination in a Thin Layer

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Received: May 21, 2001; In Final Form: September 17, 2001

This paper analyzes the small signal ac impedance of electron diffusion and recombination in a spatially restricted situation with application in systems such as porous TiO₂ nanostructured photoelectrodes and intrinsically conducting polymers. It is shown that the diffusion–recombination model with the main types of boundary conditions assumes a finite set of possible behaviors in the frequency domain, which are classified according to relevant physical parameters. There are four possible cases: (i) the impedance of finite diffusion with reflecting boundary, (ii) the impedance of finite diffusion with absorbing boundary, (iii) the impedance of diffusion–reaction in semiinfinite space or Gerischer impedance, and (iv) the impedance that combines Warburg response at high frequency and a reaction arc at low frequency. The generality of the approach is discussed in terms of the spatial distribution of the electrochemical potential or quasi-Fermi level and also in terms of the transmission line representation. An extension is considered to the diffusion in lithium intercalation electrodes coupled to a homogeneous solid-state reaction. The connection is established with other frameworks for the description of transport and reaction in electrochemical systems.

1. Introduction

The nanostructured TiO₂-based dye-sensitized photoelectrochemical cell is receiving a great deal of attention as a possible candidate for converting solar energy into electricity on a large scale.¹ A diffusion scheme has been adopted in the analysis of this system for describing the transport of photoexcited electrons.^{2–4} In general, diffusion-controlled processes occur in a variety of systems that are both technologically important and scientifically appealing, such as intercalation electrodes for rechargeable batteries and electrochromic displays, semiconductor *p–n* junctions, and intrinsically conducting polymers. These systems are studied in a number of fields including electrochemistry, photoelectrochemistry, solid-state electronics, and solid-state ionics.

The ac impedance technique is widely used in these fields because of its sensitivity and its ability to separate the different processes involved in these complex materials and devices. As is well-known, semiinfinite diffusion appears in the frequency domain in the form

$$Z(i\omega) \propto (i\omega)^{-1/2} \quad (1)$$

which is called the Warburg impedance in electrochemistry. However, the impedance analysis of systems such as those mentioned requires consideration of additional aspects to characterize the transport mechanisms and extract the available information. First, different types of boundary conditions for the diffusing species are possible, depending on the electrode configuration, which influence notably the impedance response in the low-frequency range of measurement. Moreover, the diffusing species may be removed by an irreversible process such as recombination or a homogeneous reaction. In addition, the electron motion in nanoporous semiconductor electrodes and other advanced electronic materials often involves anomalous transport mechanisms^{5,6} or a distribution of trapping or recombination rates.

The literature contains a number of models that include the removal of the diffusing particles in the diffusion impedance. Models for the impedance of electron diffusion and recombination in a homogeneous environment (the compact semiconductor) were derived in the field of semiconductor devices,^{7–9} and models for ionic diffusion in electrolyte and a coupled homogeneous reaction were derived in the domain of electrochemistry.^{10–12}

Aiming to derive a series of improved models for the analysis of advanced devices, we have developed recently a first approach to the impedance of anomalous diffusion mechanisms in electrochemical systems.⁶ However, this report considered only tangentially the questions of recombination and trapping. Furthermore, the impedance of electron transport by diffusion with recombination is well-understood in some cases,^{7–9} but these studies^{7–9} examined only the configuration usually found in solid-state devices, which adopts an absorbing boundary condition corresponding to an ohmic contact. In the analysis of porous semiconductor electrodes, it is necessary to consider a reflecting boundary condition at the outer edge of the porous film.

Therefore, we have in this paper elaborated a general formulation of impedance models for electron diffusion and recombination in a thin layer with the different boundary conditions covering most of the cases of interest for electronic and electrooptic materials and electrodes. An extension of the model to ion diffusion is provided here as well, considering the diffusion in lithium intercalation electrodes coupled to a homogeneous solid-state reaction.¹³ In a separate article, the impedance measurements of porous TiO₂ nanostructured electrodes are interpreted on the basis of the present theory.¹⁴ A more general analysis that relates the anomalous transport mechanisms to a multiple trapping scheme is currently being developed.

Section 2 lays out the basis of the treatment, as a preliminary step for the frequency study, considering the diffusion–recombination equation and the spatial distribution of quantities

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in the steady state, both for a porous semiconductor electrode and a compact semiconductor. Section 3 shows the derivation of the impedance models. In section 4, these models are rephrased as transmission lines. The analysis in section 5 determines the behaviors in the frequency domain, and a classification according to the relevant physical parameters. In Appendix 1, the general conditions of application of the models are discussed in terms of the spatial variations of the quasi-Fermi level. Appendix 2 analyzes more deeply the similarity of the diffusion–recombination model with models for porous electrodes based on transport by drift in the electrical field. This connection was mentioned but not proved in a previous work.¹⁵

2. General Diffusion–Recombination Equations, the Boundary Conditions, and the Distribution of Carriers in the Steady State

2.1. Formulation of the Diffusion–Recombination Scheme.

Diffusion theory starts off from two equations, the continuity equation and the constitutive equation. The continuity equation is a fundamental conservation law relating the time variation of the number density, n , to the macroscopic particle current, J :

$$\frac{\partial n}{\partial t} = -\frac{\partial J}{\partial x} \quad (2)$$

The constitutive equation (or Fick's law) is a phenomenological equation relating the flux, J , to the gradient of concentration, n , through the diffusion coefficient, D :

$$J = -D \frac{\partial n}{\partial x} \quad (3)$$

When combined with the continuity equation, eq 3 gives the phenomenological diffusion equation or Fick's second law:

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2} \quad (4)$$

If we consider that an irreversible first-order reaction removes the diffusing substance at a rate $k(n - n_0)$, where k is a constant and n_0 is an equilibrium concentration, the equation of conservation becomes

$$\frac{\partial n}{\partial t} = -\frac{\partial J}{\partial x} - k(n - n_0) \quad (5)$$

Assuming that the flux of the reacting species is described by eq 3, the diffusion equation adopts the form

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2} - k(n - n_0) \quad (6)$$

The diffusion–recombination eq 6 is useful in the modeling of a wide variety of situations. Here, we adopt this scheme, which covers the following instances, among others: the diffusion of an ionic species coupled with a homogeneous reaction in electrochemical systems, the transport and recombination of a minority electronic species in solid-state semiconductor devices such as the p – n junction diode,⁷ and the electron transport and recombination in nanostructured semiconductor electrodes. In these last two areas, eq 5 would be usually written in terms of the electron lifetime,

$$\tau_n = k^{-1} \quad (7)$$

2.2. Analysis in the Steady State and Boundary Conditions. In the steady state, the excess electron concentration in the diffusion–recombination model is determined by the equation

$$\frac{\partial^2 n}{\partial x^2} - \frac{n - n_0}{L_n^2} = 0 \quad (8)$$

which has been written using the electron diffusion length

$$L_n = (D\tau_n)^{1/2} \quad (9)$$

The boundary conditions that complement eq 8 are now discussed considering two specific examples. These two examples illustrate the class of situations described by the impedance models discussed in this paper, although a more complete discussion concerning the conditions of application is provided in Appendix 1. In brief, an applied potential difference determines the carrier concentration at one edge of the diffusion region. At the other edge, the carriers may be either blocked or extracted. These boundary conditions are denoted here as reflecting and absorbing, respectively. This nomenclature arises from the random walk picture, in which these boundary conditions describe the reflection or absorption of the walker upon encountering a wall at $x = L$.^{16,17}

Although for the purpose of illustration the two systems considered in the following are treated as essentially similar concerning the diffusion of the electronic species, some important differences should be pointed out. In the nanostructured electrodes, the semiconductor usually contains a single kind of electronic carriers, namely, electrons for dye-sensitized TiO₂, and recombination is synonymous to interfacial charge transfer at the oxyde/electrolyte interface. In solid-state p – n junctions, both electrons and holes are present, recombination involves a pair of the oppositely charged species, and diffusion concerns the minority carrier.

The Porous Semiconductor Electrode. Figure 1a shows an electrochemical configuration in which electrons with concentration n are injected at the contact between a porous semiconductor network and the conducting substrate ($x = 0$).² Electrons diffuse and recombine in the film volume ($0 < x < L$), and the transport is blocked at the outer edge of the film ($x = L$), where the condition $J = 0$ holds or, in other words,

$$\frac{\partial n}{\partial x} = 0 \quad (x = L) \quad (10)$$

which is the reflecting boundary condition.

The electric current i at the electrode/substrate boundary is given by

$$i = -qAD \frac{\partial n}{\partial x} \quad (x = 0) \quad (11)$$

where q is the elementary charge and A is the electrode area. In the nanoporous system permeated with a redox electrolyte, the equilibrium value, n_0 , is determined by equilibrium electron exchange at the oxyde/electrolyte interface and the excess electrons are pumped into the film by an overvoltage, E , that raises the concentration at the surface to n_s , see Figure 1a. (The overvoltage here means the increase of the electrostatic potential at the conducting substrate with respect to the equilibrium redox potential, see Appendix 1 and Figure 7.) In general, there is a unique relationship between the overvoltage, E , and the surface concentration, n_s , which can be stated as

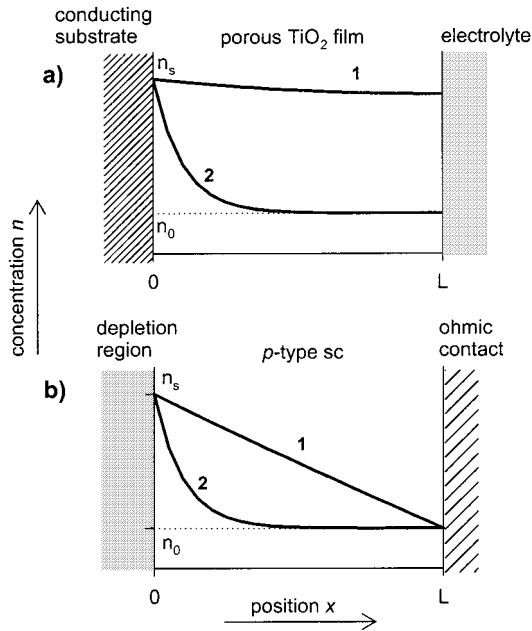


Figure 1. Excess concentration in the stationary condition for (a) electrons injected at the substrate to a porous semiconductor film permeated with a redox electrolyte (the electrons are blocked at the outer edge of the film) and (b) electron minority carriers in the p region of the semiconductor p - n junction (the electrons are extracted at the ohmic contact). In both cases, curve 1 is for $L_n = 2L$ and curve 2 for $L_n = 0.1L$.

$$n = n_s = n_0 f(E) \quad (x = 0) \quad (12)$$

where the form $f(E)$ depends on the system's thermodynamics, as explained in Appendix 1, the equilibrium condition $f(0) = 1$ being satisfied. In the ideal case, it is described by Boltzmann's statistics or Nernst expression

$$f(E) = \exp(qE/(k_B T)) \quad (13)$$

and this last equation is usually applied in the nanostructured system of Figure 1a, at least in the simplest approach, which neglects the effect of band unpinning by charging of surface states.

From eqs 8, 11, and 13, the following distribution of electrons in the porous network is found:

$$\bar{n} = n_0 + n_0 [f(\bar{E}) - 1] [\cosh(x/L_n) - \coth(L/L_n) \sinh(x/L_n)] \quad (14)$$

where the overbar denotes the steady state. It is noted that if $L_n/L \ll 1$ (curve 2 in Figure 1a) the excess electrons disappear before they can reach the boundary.

Diffusion of Electrons in the Compact Semiconductor. The other system, shown in Figure 1b, is the neutral p region of a semiconductor p - n junction diode. Here, the number of electrons injected at $x = 0$ is determined by the voltage drop across the space-charge region at the junction, and the concentration at the surface is described also by eqs 12 and 13. In this system, however, all of the electrons that reach the substrate are extracted at the ohmic contact so that at this contact

$$n = n_0 \quad (x = L) \quad (15)$$

This is the absorbing boundary condition, which leads to the expression

$$\bar{n} = n_0 + n_0 [f(\bar{E}) - 1] [\cosh(x/L_n) - \tanh(L/L_n) \sinh(x/L_n)] \quad (16)$$

This distribution of electrons is plotted in Figure 1b. Again it is noted that if $L_n/L \ll 1$ the diffusing electrons do not reach the contact and the concentration in curve 2 of Figure 1b is the same as that of Figure 1a. Clearly, if $L_n/L \ll 1$, the boundary at $x = L$ is irrelevant and the system behaves as semiinfinite. This result will be recalled below in the frequency study.

Current and Resistance in the Steady State. The electrical current associated with the diffusion mechanism is given by eq 11. For the reflecting boundary condition, it is found that the dc current is

$$\bar{i} = \frac{qADn_0}{L_n} [f(\bar{E}) - 1] \tanh(L/L_n) \quad (17)$$

and therefore the dc resistance $R_{dc} = d\bar{E}/d\bar{i}$ has the expression

$$R_{dc} = \frac{L_n \coth(L/L_n)}{qADn_0 f'(\bar{E})} \quad (18)$$

Similarly for the absorbing boundary condition,

$$\bar{i} = \frac{qADn_0}{L_n} [f(\bar{E}) - 1] \coth(L/L_n) \quad (19)$$

and

$$R_{dc} = \frac{L_n \tanh(L/L_n)}{qADn_0 f'(\bar{E})} \quad (20)$$

3. Derivation of the Impedance Models

3.1. Diffusion in a Thin Layer. We revise in this section the basic ac impedance models for diffusion in a thin layer in the absence of recombination, which is a suitable preliminary step and also a particular case of the general problem treated thereafter including the recombination.

The calculation of the linear impedance uses small amplitude oscillating quantities, here denoted by a tilde, superimposed to a given stationary condition (i.e., $n = \bar{n} + \tilde{n}$, $J = \bar{J} + \tilde{J}$, etc). The diffusion eqs 2 and 3 lead to the equations

$$\frac{\partial \tilde{n}}{\partial t} = - \frac{\partial \tilde{J}}{\partial x} \quad (21)$$

$$\tilde{J} = -D \frac{\partial \tilde{n}}{\partial x} \quad (22)$$

The ac modulated quantities are obtained by Laplace transform, $C(s) = \mathcal{L}[\tilde{n}]$, $j(s) = \mathcal{L}[\tilde{J}]$, where s is the Laplace variable related to the angular frequency by $s = i\omega$, and $\omega = 2\pi f$, f being the frequency. The transformation gives the expressions

$$sC = - \frac{\partial j}{\partial x} \quad (23)$$

$$j = -D \frac{\partial C}{\partial x} \quad (24)$$

The concentration at a given frequency is determined by the equation

$$\frac{\partial^2 C}{\partial x^2} - \frac{1}{\lambda^2} C = 0 \quad (25)$$

where

$$\lambda(s) = \left(\frac{\omega_d}{s}\right)^{1/2} L \quad (26)$$

Here, the frequency

$$\omega_d = D/L^2 \quad (27)$$

is the characteristic frequency of diffusion in a finite layer, which corresponds to the transit time, t , for a diffusing particle injected at $x = 0$ to cover a distance, L . (More precisely, in one-dimensional diffusion, $L^2 = 6Dt$ so that the angular frequency of transit is $\omega_t = 6\omega_d$, which corresponds to the frequency $f_t = 6\omega_d/(2\pi) \approx \omega_d$.)

At the injecting boundary ($x = 0$), both the ac potential and the current can be related to the oscillating concentration. The modulation of concentration by the external voltage is given by

$$\tilde{E} = \frac{d\tilde{E}}{d\tilde{n}} \tilde{n} \quad (x = 0) \quad (28)$$

and from eq 12,

$$\tilde{E} = \frac{1}{n_0 f'(\tilde{E})} \tilde{n} \quad (x = 0) \quad (29)$$

By eq 11, the ac current is expressed as

$$\tilde{i} = -qAD \frac{\partial \tilde{n}}{\partial x} \quad (x = 0) \quad (30)$$

The linear impedance is obtained from the equation

$$Z(s) = \frac{U(s)}{I(s)} \quad (31)$$

where $U(s) = \mathcal{L}[\tilde{E}]$ and $I(s) = \mathcal{L}[\tilde{i}]$. Using eqs 29 and 30, one gets

$$Z(s) = R_W \frac{D}{L} \frac{C(s)}{j(s)} \quad (x = 0) \quad (32)$$

where the diffusion resistance is defined as

$$R_W = \frac{L}{qADn_0 f'(\tilde{E})} \quad (33)$$

This resistance is not generally equal to the dc resistance (see below, eqs 50 and 51). Another useful parameter is the free charge capacitance defined as

$$C_f = \frac{1}{R_W \omega_d} \quad (34)$$

In the special case of the Nernstian behavior (or Boltzmann statistics), R_W and C_f adopt particularly simple expressions, as one has

$$f'(\tilde{E}) = \frac{q}{k_B T} f(\tilde{E}) \quad (35)$$

so that eq 33 takes the form

$$R_W = \frac{k_B T L}{q^2 A D n_s} = \frac{L}{A \sigma_s} \quad (36)$$

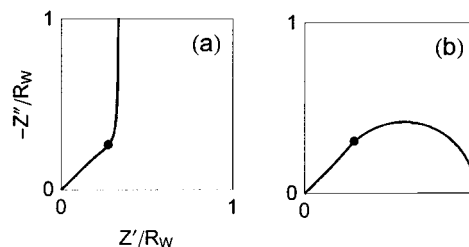


Figure 2. Complex plots of the impedance model for ordinary diffusion in a layer of thickness L : (a) reflecting boundary condition, $\partial \tilde{n} / \partial x = 0$ at $x = L$; (b) absorbing boundary condition, $\tilde{n} = 0$ at $x = L$. $\omega_d = 1 \text{ rad s}^{-1}$, and the marked points correspond to the frequency (Hz) $f = \omega_d$.

where σ_s is the conductivity at the boundary and eq 34 may be written as a differential capacitance

$$C_f = \frac{d}{dE}(ALqn_s) \quad (37)$$

which is also denoted the diffusion capacitance^{18,19} and the conduction band capacitance.^{20,21}

The reflecting boundary condition for the small ac oscillating concentration is

$$\frac{\partial C}{\partial x} = 0 \quad (x = L) \quad (38)$$

while the absorbing boundary condition is described as

$$C = 0 \quad (x = L) \quad (39)$$

These two boundary conditions are specialized cases of a more general condition defined in terms of a specific impedance at this boundary.^{19,22} However, in this paper, only the standard conditions of eqs 38 and 39 will be used.

The expression of the impedance follows readily from inserting the solution of eq 25, with either of the boundary conditions, into eq 32. The result, for the reflecting boundary, is

$$Z = R_W (i\omega/\omega_d)^{-1/2} \coth[(i\omega/\omega_d)^{1/2}] \quad (40)$$

This impedance function is illustrated in Figure 2a. The two regimes of behavior seen in the figure are separated by the frequency ω_d . For $\omega \gg \omega_d$, the particles will not sense the boundary at $x = L$ so that the system will behave as semiinfinite, that is, eq 1 or, more precisely,

$$Z = R_W (i\omega/\omega_d)^{-1/2} \quad (41)$$

On the other hand, at low frequency, the response is

$$Z = \frac{1}{3} R_W + \frac{1}{iC_f \omega} \quad (42)$$

For the absorbing boundary condition, one gets

$$Z = R_W (i\omega/\omega_d)^{-1/2} \tanh[(i\omega/\omega_d)^{1/2}] \quad (43)$$

This model is illustrated in Figure 2b, and one obtains eq 41 again at high frequency, while at low frequency, the admittance is given by

$$Z^{-1} = \frac{1}{R_W} + \frac{1}{3} i C_f \omega \quad (44)$$

The fact that the diffusion appears as semiinfinite at high frequencies is related to the penetration of the ac concentration wave. Through the use of eq 26, the condition $\omega \gg \omega_d$ can be expressed in terms of the penetration length and the thickness of the diffusion layer: $\lambda \ll L$.

3.2. Impedance of Diffusion and Recombination (or Diffusion and Coupled Reaction). The eqs 3 and 6 of the diffusion–recombination model, for small amplitude oscillating quantities, superimposed to a given stationary state, turn into

$$\frac{\partial \tilde{n}}{\partial t} = -\frac{\partial \tilde{J}}{\partial x} - k\tilde{n} \quad (45)$$

$$\tilde{J} = -D \frac{\partial \tilde{n}}{\partial x} \quad (46)$$

and the Laplace transform gives

$$(s + k)C = -\frac{\partial j}{\partial x} \quad (47)$$

$$j = -D \frac{\partial C}{\partial x} \quad (48)$$

The expression determining the spatial distribution of the ac wave of concentration is the same as eq 25, where

$$\lambda(s) = \left(\frac{\omega_d}{s + k} \right)^{1/2} L \quad (49)$$

The diffusion resistance, R_W , and capacitance are defined in the same way as above. The dc resistance of eq 18, for the reflecting case, may be expressed as

$$R_{dc} = \frac{L_n \coth(L/L_n)}{L} R_W \quad (50)$$

and for the absorbing case, from eq 20,

$$R_{dc} = \frac{L_n \tanh(L/L_n)}{L} R_W \quad (51)$$

The impedance for the reflecting boundary condition is^{11,12}

$$Z = \left(\frac{R_W R_k}{1 + i\omega/\omega_k} \right)^{1/2} \coth[(\omega_k/\omega_d)^{1/2} (1 + i\omega/\omega_k)^{1/2}] \quad (52)$$

and for the absorbing boundary condition⁷ is

$$Z = \left(\frac{R_W R_k}{1 + i\omega/\omega_k} \right)^{1/2} \tanh[(\omega_k/\omega_d)^{1/2} (1 + i\omega/\omega_k)^{1/2}] \quad (53)$$

In these expressions, we have introduced the characteristic frequency of the reaction or recombination process:

$$\omega_k = k \quad (54)$$

Furthermore the resistance R_k corresponds to the additional loss introduced in the system by the homogeneous reaction or recombination process:

$$R_k = \frac{\omega_d}{k} R_W \quad (55)$$

and R_k is called henceforth the reaction resistance.

It should be emphasized that the impedance functions of diffusion in eqs 40 and 43 have two independent parameters

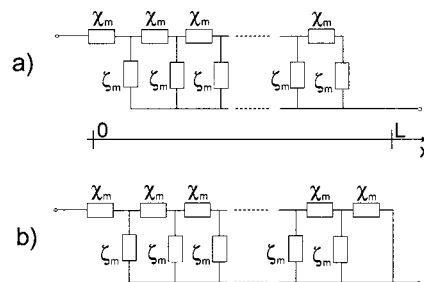


Figure 3. General transmission line representation of the diffusion impedance: (a) reflecting boundary condition; (b) absorbing boundary condition.

(R_W , ω_d), whereas the impedances of diffusion–recombination in eqs 52 and 53 have three (for instance, R_W , ω_d , and k). Furthermore, to avoid a possible confusion of forms, it is noted that in the area of solid-state electronics eq 53 is often expressed in terms of the dc resistance of eq 51, as follows:⁷

$$Z = R_{dc} \frac{\tanh\{[(L/L_n)^2 + i\omega L^2/D_n]^{1/2}\}}{(1 + i\omega\tau_n)^{1/2} \tanh[L/L_n]} \quad (56)$$

4. Transmission Line Representation of the Impedance

The impedance response of diffusion may be represented as a distributed equivalent circuit (a transmission line). This equivalent circuit representation was noted in the area of solid-state electronics²³ and subsequently in electrochemistry.^{19,24,25} Here, we show the expression of the impedance models of diffusion–recombination in terms of transmission lines.

The representation is established by the following expressions:¹⁹

$$i_m(x) = qA j \quad (57)$$

$$\phi_m(x) = \left(\frac{dE}{dc} \right)_0 C \quad (58)$$

which convert the flux to electrical current in the line i_m and the concentration to voltage in the line ϕ_m . For the general transmission lines shown in Figure 3, these quantities obey the equations¹⁵

$$\frac{\partial i_m}{\partial x} = -\frac{1}{Z_m} \phi_m \quad (59)$$

$$\frac{\partial \phi_m}{\partial x} = -\chi_m i_m \quad (60)$$

Here, χ_m is an impedance per unit length ($\Omega \text{ m}^{-1}$), and Z_m is an impedance–length ($\Omega \text{ m}$) corresponding to the whole electrode area, A . According to the correspondence, the impedance of the transmission line

$$Z = \frac{\phi_m(0)}{i_m(0)} \quad (61)$$

equals the impedance of diffusion in a layer of thickness L with diffusion overvoltage at $x = 0$.

In the transmission line, the boundary condition at $x = L$ is represented by a specific impedance at that point.^{19,26} Considering first the reflecting boundary condition of eq 20, which appears as an open circuit at $x = L$ in Figure 3a, it can be shown from eqs 59 and 60 that the impedance has the form

$$Z = (\zeta_m \chi_m)^{1/2} \coth[L(\chi_m/\zeta_m)^{1/2}] \quad (62)$$

The absorbing boundary condition of eq 21 is represented by a short circuit at $x = L$,¹⁹ as shown in Figure 3b. The impedance of the line is in that case

$$Z = (\zeta_m \chi_m)^{1/2} \tanh[L(\chi_m/\zeta_m)^{1/2}] \quad (63)$$

Therefore, the impedance of any diffusion theory that consists of equations similar to eqs 59 and 60 can be pictured as a transmission line, while the specific form of the elements χ_m and ζ_m in the line depends on the specific features of the diffusion model. A number of advanced transmission line models for anomalous diffusion have been reported recently.⁶

For simple diffusion (without reaction), comparing eqs 23 and 24 to eqs 59 and 60, one gets

$$\chi_m = r_m \quad (64)$$

$$\zeta_m = \frac{1}{c_m s} \quad (65)$$

where

$$r_m = \frac{R_W}{L} \quad (66)$$

$$c_m = \frac{C_f}{L} = \frac{L}{R_W D} \quad (67)$$

This is the familiar transmission line^{19,22} containing distributed resistors r_m and capacitances c_m shown in Figures 4a and 4b.

For diffusion and recombination, eq 48 gives again eq 64, and eq 47 gives for the ζ -impedance in this case

$$\zeta_m = \frac{r_k}{1 + i r_k c_m \omega} \quad (68)$$

where the c_m is the distributed capacitance of eq 67 and the new element, with respect to ordinary diffusion, is the distributed reaction resistance given by

$$r_k = L R_k = \frac{1}{k C_m} \quad (69)$$

which is connected in parallel to c_m , as shown in Figures 4c and 4d.

5. Classification and Properties of the Impedance Models for Diffusion and Reaction

The inspection of eqs 8 and 25 shows that the ac concentration C in the diffusion–recombination scheme is distributed in space in the same way as the excess concentration $\bar{n} - n_0$ is distributed in the dc case (Figure 1). However, for the ac concentration the penetration length λ is a function of frequency, eq 49. This function is usually termed L_n^* in the literature of solid-state electronics.¹⁸

The maximum value of $\lambda(\omega)$ occurs at frequency zero, and it is $\lambda(\omega=0) = L_n$. Therefore, if $L_n < L$, one has $\lambda < L$ at all frequencies, and in consequence, as shown in more detail below, a unique diffusion–reaction impedance model exists for this case independently of the boundary condition, as also found above in the study of the excess concentration in the steady state.

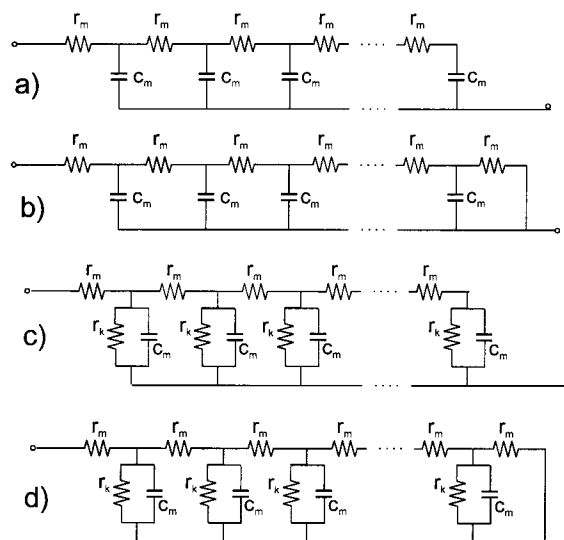


Figure 4. Transmission line representation of the diffusion impedance: (a) simple diffusion with the reflecting boundary condition; (b) simple diffusion with the absorbing boundary condition; (c) diffusion coupled with a homogeneous reaction with the reflecting boundary condition; (d) diffusion coupled with a homogeneous reaction with the absorbing boundary condition.

More generally, the behaviors with respect to the variation of the frequency are determined by the relative strength of some physicochemical parameters in the system, as expressed in the following relationships:

$$\frac{R_k}{R_W} = \frac{\omega_d}{\omega_k} = \left(\frac{L_n}{L}\right)^2 \quad (70)$$

The different cases according to the value of eq 70 and the boundary conditions are discussed in the following paragraphs.

5.1. Reflecting Boundary Condition. We discuss the properties of eq 52, and the different cases are shown in Figure 5. First, it is noted that the limiting case, $R_k \rightarrow \infty$, leads to the simple diffusion model of eq 40, shown in curve 1 of Figure 5. In other words, the resistor, r_k , in Figure 4c is an open circuit and the transmission line turns into that of Figure 4a.

For a finite reaction resistance R_k , two different cases occur, depending on the quotient of eq 70. If the reaction resistance is much larger than the diffusion resistance ($R_k \gg R_W$), then the impedance is given at high frequency ($\omega \gg \omega_d$) by eq 41 and at low frequency ($\omega \ll \omega_d$) by the expression

$$Z = \frac{1}{3} R_W + \frac{R_k}{1 + i\omega/\omega_k} \quad (71)$$

Therefore, the impedance (curve 2 in Figure 5) has a small Warburg part at high frequency and a large arc at low frequency, the latter corresponding to the recombination or reaction process, which is much slower than diffusion through the layer in this case ($\omega_d \gg \omega_k$). The location of these characteristic frequencies in the impedance plot is shown in Figure 5. Around the transition frequency, ω_d , the impedance behaves as eq 40.

In the other case, $R_k \ll R_W$, eq 52 leads to the function

$$Z = \left(\frac{R_W R_k}{1 + i\omega/\omega_k} \right)^{1/2} \quad (72)$$

In this case, shown in curve 3 of Figure 5, the recombination time is shorter than the time for diffusion across the layer ($\omega_k \gg \omega_d$) and the concentration profile decays before the species

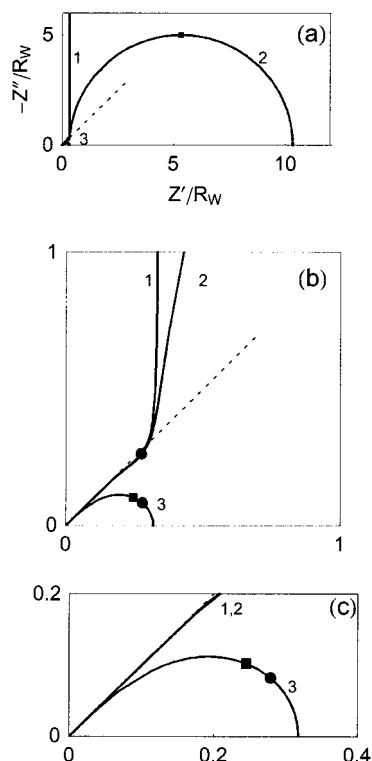


Figure 5. Complex plots of the impedance model for diffusion coupled with a homogeneous reaction with the reflecting boundary condition, $\partial \tilde{n}/\partial x = 0$ at $x = L$. $\omega_d = 1 \text{ rad s}^{-1}$ in all cases. Panels b and c show consecutive enlargements of panel a. Curve 1 is for no reaction, $R_k \rightarrow \infty$, that is, the same as Figure 3a. In curve 2, $R_k = 10R_W$, and thus, $\omega_k = 0.1 \text{ rad s}^{-1}$. In curve 3, $R_k = 0.1R_W$, and thus, $\omega_k = 10 \text{ rad s}^{-1}$. The marked points correspond to frequencies (Hz) $f = \omega_d$ (●) and $f = \omega_k/(2\pi)$ (■).

can reach the boundary at $x = L$ (i.e., $L_n \ll L$). Therefore, eq 72 corresponds to diffusion and recombination in semiinfinite space, although the same behavior can obviously occur in very thin layers where the diffusing particles react heavily. The model of eq 72 has been called the Gerischer impedance^{12,27} after its first derivation,¹⁰ and its experimental verification in gas diffusion electrodes has been reported several times.^{27,28}

It is noted that the cases distinguished according to eq 70 provide rather different results for the dc resistance:

$$R_{dc} = \frac{1}{3}R_W + R_k \quad (R_k \gg R_W) \quad (73)$$

$$R_{dc} = (R_W R_k)^{1/2} \quad (R_W \gg R_k) \quad (74)$$

5.2. Absorbing Boundary Condition. Here, we discuss the properties of eq 53, and the different cases are shown in Figure 6. First of all, we note that the limiting case, $R_k \rightarrow \infty$, gives the simple diffusion model of eq 43, shown in curve 1 of Figure 6. For a finite reaction resistance, R_k , there are two cases as determined by eq 70.

For $R_k \gg R_W$, eq 53 is approximately equal to eq 43, as seen in curve 2 of Figure 6. The reason that the effect of the reaction is suppressed in this case can be noticed in the transmission line of Figure 4d. When r_k is large, the conductive path at the boundary ($x = L$) becomes dominant and Figure 4d reduces to Figure 4b. (However the dc resistance in Figure 6 is slightly less for curve 2 than that for curve 1, owing to the additional path through the r_k 's.) This result can be proved more rigorously.²⁹ Therefore, in an electronic system, when the diffusion length is larger than the diffusion region ($L_n \gg L$), the effect of

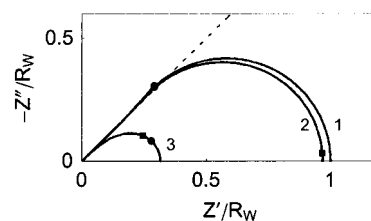


Figure 6. Complex plots of the impedance model for diffusion coupled with a homogeneous reaction with the absorbing boundary condition, $\tilde{n} = 0$ at $x = L$. $\omega_d = 1 \text{ rad s}^{-1}$ in all cases. Curve 1 is for no reaction, $R_k \rightarrow \infty$, that is, the same as Figure 3b. In curve 2, $R_k = 10R_W$, and thus, $\omega_k = 0.1 \text{ rad s}^{-1}$. In curve 3, $R_k = 0.1R_W$, and thus, $\omega_k = 10 \text{ rad s}^{-1}$. The marked points correspond to frequencies (Hz) $f = \omega_d$ (●) and $f = \omega_k/(2\pi)$ (■).

recombination is insignificant. This has been confirmed by the impedance measurement of a p^+-n diode in which the lower doped n region is narrow.³⁰

For the other case, $R_W \gg R_k$, the boundary condition is irrelevant ($L_n \ll L$), as already argued above, and eq 53 gives the Gerischer impedance of eq 72. This result has been emphasized in the field of semiconductor devices.^{7,9,18} If $R_k \gg R_W$, the dc resistance is approximately $R_{dc} = R_W$, while it is given by eq 74 if $R_W \gg R_k$.

6. Discussion and Conclusions

The linear impedance of the diffusion–recombination or diffusion–reaction scheme for voltage control at one macroscopic boundary and either a blocking or ohmic contact at the other boundary has been solved, and the general expressions of the impedance are given in eqs 52 and 53. Despite the apparent complexity of these expressions, the possible line shapes reduce to four cases, namely, (i) the standard impedance of finite diffusion with reflecting boundary, Figure 2a, (ii) the standard impedance of finite diffusion with absorbing boundary, Figure 2b, (iii) the impedance of diffusion–reaction in semiinfinite space, or Gerischer impedance, curve 3 of Figure 5, or (iv) the impedance that combines Warburg response at high frequency and a reaction arc at low frequency, curve 2 in Figure 5. The actual occurrence of these shapes is determined by the boundary condition and by the value of the factor in eq 70.

At sufficiently high frequency, it holds that $s \gg k$ so that the penetration length of diffusion and reaction, eq 49, adopts the form of ordinary diffusion, eq 26. If, in addition $\omega \gg \omega_d$ at these high frequencies, then the impedance of diffusion–recombination behaves as in semiinfinite diffusion (without reaction), i.e., eq 41. These considerations provide two final conclusions:

(i) Diffusion, either with recombination or not, always presents a region of slope 1 in the complex plane plot at high frequency, and this can be checked in Figures 5 and 6. However, the actual experimental observance of the regime where $Z(i\omega) \propto (i\omega)^{-1/2}$ depends on two factors, namely, the window of frequencies used in the measurement and the requirement that other kinetic processes (such as a sluggish electron injection at $x = 0$) do not overlap the diffusion dynamics at these high frequencies.

(ii) The diffusion–recombination model discussed here cannot give the behavior of *anomalous* diffusion, discussed elsewhere,⁶ which is characterized by a slope different than 1 at high frequency, i.e., $Z(i\omega) \propto (i\omega)^{-\beta/2}$ with $0 < \beta < 2$.

Acknowledgment. Discussions with L. M. Peter, G. Garcia-Belmonte, and F. Fabregat-Santiago are gratefully acknowl-

edged. This work was supported by la Comisión Interministerial de Ciencia y Tecnología under Project PB98-1045.

Appendix 1. General Conditions of Application

In general, the driving force for transport is the gradient of the electrochemical potential, which for electrons is referred to as the quasi-Fermi level E_{Fn} so that the particle flux is given by

$$J_n = n\nu_n \left[-\frac{1}{q} \frac{\partial E_{Fn}}{\partial x} \right] \quad (A1.1)$$

where $(-1/q)(\partial E_{Fn}/\partial x)$ is the driving force and ν_n is the mobility, related to the electron diffusion coefficient D_n by

$$\nu_n = \frac{qD_n}{k_B T} \quad (A1.2)$$

The quasi-Fermi level for electrons in a solid material (such as the porous semiconductor film permeated with a redox electrolyte) contains contributions both from the local value of the electrostatic potential, φ , and from the chemical potential, μ , as follows:

$$E_{Fn} = E_{Fn}^0 - q(\varphi - \varphi^0) + \mu \quad (A1.3)$$

Here, E_{Fn}^0 is the equilibrium Fermi level and φ^0 is the electrostatic potential of the solid phase in equilibrium with the redox electrolyte. In the nanoporous system, the potential in the semiconductor, φ , can denote either the inner or Galvani potential or the energy of the conduction band edge, $E_c = -q\varphi$, that is, it can be expressed either in the scale of energy of electrochemistry (with respect to standard electrode) or solid-state physics (with respect to the vacuum level). The chemical potential is related to the activity of the electrons, a_n , by

$$\mu = \mu^0 + k_B T \ln \frac{a_n}{a_n^0} \quad (A1.4)$$

In the impedance technique, the electrical potential difference that is monitored externally corresponds to the difference of electrochemical potential or quasi-Fermi level of electrons at the outer contacts. However, such external potential difference may affect the local value of the quasi-Fermi level into the measured system both as a variation of the local electrostatic potential φ and as a variation of the activity a_n or concentration n . A gradient of the former gives rise to the drift force, while a gradient of the latter leads to the diffusion force.

Here, it is assumed that the electrostatic potential remains at the equilibrium level, $\varphi = \varphi^0$, in the region $0 < x < L$ (diffusion). One can alternatively say that the level of the conduction band edge is homogeneous in the film volume. As illustrated in Figure 7, the applied potential E raises the quasi-Fermi level of electrons into the film at $x = 0$. More specifically, the voltage E in the substrate is more negative than the equilibrium $E = 0$ (redox potential), and the substrate/semiconductor junction is assumed to be not rectifying so that the quasi-Fermi level is continuous at the junction. Therefore at $x = 0^-$, one has $\Delta E_{Fn} = -qE$, while at $x = 0^+$, it holds that $\Delta E_{Fn} = \Delta\mu$, and in consequence

$$a_n = a_n^0 \exp(-qE/(k_B T)) \quad (x = 0) \quad (A1.5)$$

The expression of this last equation in terms of the concentration,

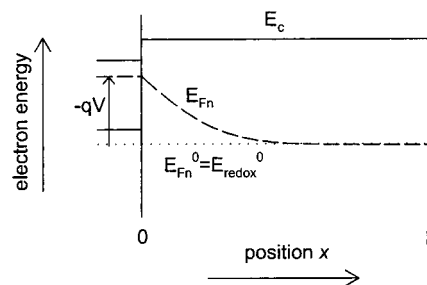


Figure 7. Energy scheme showing the variation of the quasi-Fermi level E_{Fn} relative to the equilibrium value E_{Fn}^0 for an applied potential $V < 0$. The increase of the quasi-Fermi level is due to an increase of the electron concentration in $0 < x < L$ (corresponding to curve 2 in Figure 1b), while the edge of the conduction band E_c remains pinned.

n , leads to eq 12. In the case that the electrons obey Boltzmann statistics, $a_n = n$ gives the ideal form in eq 13 (with a minus sign in the argument).

This formulation is rather general and can be extended readily, for instance, to the diffusion of ions coupled to a homogeneous reaction. A case in point is the diffusion of lithium ions in a metal oxide electrochromic film, because it has been suggested recently^{13,31} that an immobilization process is coupled to the solid-state diffusion of Li^+ . Such an ion-trapping process can be described in a preliminary approach as a solid-state reaction. In this type of model, the ions are injected from an ion-rich solution ($x = 0$), they diffuse and react in the film volume ($0 < x < L$), and they are blocked at the contact between the active film and the substrate ($x = L$). At the film/substrate boundary, the condition $J = 0$ holds. This latter boundary is usually transparent to electrons, which compensate the charge of inserted ions so that overall neutrality of charge prevails in the film region. These electrons, however, cannot enter the liquid phase, and therefore, the electric current i at the electrode/electrolyte boundary is entirely ionic, and it is given by eq 11 (where n represents in this case the ionic concentration). The overvoltage, E , determines the surface concentration, n_s , according to eq 12. In the lithium intercalation compounds, $f(E)$ departs heavily from the ideal expression of eq 13.

It must be emphasized that in all cases the function $f(E)$, which conditions the parameters of the diffusion impedance, is determined by the thermodynamic properties of the active film and it is not dependent on the properties of the interface at $x = 0$, of which the only role in the present context is to translate the externally applied voltage into an increase of activity at the outer edge of the layer. The mechanism by which this occurs depends on the specific type of interface at $x = 0$. It is furthermore noted that in systems showing a considerable open circuit voltage, such as the battery cathodes, one should consider in the overvoltage the variable chemical potential of the inserted species, or back emf, namely, $E = E_{app} - E_{emf}$.^{31–33}

The increase of free energy at $x = 0$ is distributed in the layer ($0 < x < L$), but in this region, as already noted, for the diffusion approach, only the chemical potential varies with respect to the reference value. According to this assumption the eqs A1.1–A1.4 of this Appendix lead to

$$J_n = -D_n \frac{\partial \ln a_n}{\partial \ln n} \frac{\partial n}{\partial x} \quad (A1.6)$$

This expression has the form of the phenomenological eq 3, or Fick's law, with an effective diffusion coefficient

$$D = \frac{\partial \ln a_n}{\partial \ln n} D_n \quad (\text{A1.7})$$

which is denoted as the chemical diffusion coefficient, in some cases.^{25,34} According to eq A1.7, the effective diffusion coefficient depends on concentration and Fick's law can be used provided that the thermodynamic factor $\partial \ln a_n / \partial \ln n$ can be considered constant. This was assumed in the text so that eq 3 holds with a constant D .

Besides the simple diffusion approach assumed here, there are other treatments taking into account a coupled electron-ion transport in electrochemical systems³⁵ and, similarly, ambipolar diffusion effects in compact semiconductors. These treatments result in similar impedance functions as those given here but with a different expression for the characteristic frequency of transport.³⁵

Appendix 2. Degeneracy of Impedance Models Involving Transport

In a previous report, we stated that the results of the diffusion-recombination model discussed here are equivalent, as far as the small signal ac impedance is concerned, to a model for porous electrodes in which the transport is by drift in the electrical field and the reaction is at the pore surface.¹⁵ From the results of ref 15 and those presented here, this equivalence is now demonstrated.

Indeed, comparison of the eq 52 here with the eq 20 of ref 15 shows that the impedance form is the same for both models. Alternatively, one can compare the transmission line of Figure 4c here with the model 2 in Figure 2 of ref 15.

In general, as argued in the preceding Appendix, the measurement in the impedance technique involves a time-varying difference of the quasi-Fermi level at the outer contacts, and consequently, theories that do not differentiate the spatial distribution of the quasi-Fermi level provide equivalent results for the impedance. In the diffusion-recombination model, the distribution of the quasi-Fermi level in Figure 7 is from the chemical potential, while in the porous electrode model,¹⁵ that distribution is from a variation of the local electrostatic potential (an ohmic drop). However, the equations describing the spatial variation of the quasi-Fermi level in these two models are equivalent, so the resultant impedance functions are the same.

We conclude that the impedance model for diffusion and homogeneous reaction outlined above is equivalent to the model 3 of ref 15 by the following identifications: $R_w \leftrightarrow R_1$, $C_f \leftrightarrow C_3$, and $R_k \leftrightarrow R_3$ and with similar relationships for the lowercase local parameters. Therefore, the analysis of the features of the distributed impedance model in previous works^{15,36} could be applied to the diffusion-recombination model with the reflecting boundary condition developed here.

More generally, we note that models that establish a precise macroscopic theory for the local events of transport and reaction are degenerate with respect to the correspondent ac impedance because the modeling by local equations contains information that is lost when passing to the impedance, which considers

only external quantities. To distinguish which are the actual physical mechanisms, according to the different models, one has to look at the variation of the parameters in different stationary conditions.

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