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L R Evangelista[1], E K Lenzi[1], G Barbero[2] and J R Macdonald[3]

[1] Departamento di Física, Universidade Estadual de Maringá, Avenida Colombo 5790,
87020-900 Maringá, Paraná, Brazil
[2] Dipartimento di Fisica del Politecnico, Corso Duca degli Abruzzi 24, 10129 Torino, Italy
[3] Department of Physics and Astronomy, University of North Carolina, Chapel Hill, NC 27599, USA

E-mail: lre@dfi.uem.br

Abstract
The contribution of ions to the electrical impedance of an electrolytic cell limited by perfect blocking electrodes is determined by considering the role of the anomalous diffusion process and memory effects. Analytical solutions for fractional diffusion equations together with Poisson's equation relating the effective electric field to the net charge density are found. This procedure allows the construction of general expressions for the electrochemical impedance satisfying the Kramers–Kronig relations when the diffusion of ions in the cell is characterized by the usual, as well as by anomalous, behavior.

(Some figures may appear in colour only in the online journal)

1. Introduction

To a significant extent, the understanding of the role of ions on the electrical impedance of liquid and solid materials, achieved by means of several models proposed in recent years, requires a focus on the possible mechanisms underlying the participation of the ions in the process [1–13]. To describe the redistribution of ions in a weak electrolyte, upon the application of an external electric field, usually the continuum approximation is employed. The fundamental equations to be solved are then the continuity equations for the positive and negative charge carriers and Poisson's equation for the electric field across the cell [14, 15]. This is the so-called Poisson–Nernst–Planck (PNP) model. If the complex mechanisms mentioned above are to be taken into account in a more complete phenomenological scenario, the necessity to modify Fick's law and to solve a modified diffusion equation may be unavoidable. For these reasons, fractional diffusion equations have been considered as an appropriate theoretical approach to take into account the ionic redistribution effect on the impedance. The basic idea guiding this procedure is the connection usually found between fractional diffusion equations and anomalous diffusion processes [15]. Recently, Bisquert and co-workers [16–19] have investigated several models to address the electrochemical impedance of diffusion by means of fractional calculus. In more recent works [15, 20–22], we have analyzed this influence by means of a model in which the fractional drift–diffusion problem was analytically solved. Differently from previous approaches along these lines, the resulting distribution of the electric field inside the sample was determined by solving Poisson's equation.

In this paper, we present the general expression for the electrical impedance that results from a complete mathematical model based on the fractional diffusion equation of distributed order. We show that, in the appropriate limits, this expression reduces to the one obtained for the usual diffusion [23, 24] as well as to the one corresponding to a single anomalous diffusive regime [15, 20]. Subsequently, we analyze the physical meaning and the consistency of these new expressions incorporating anomalous diffusion processes to the description of the role of ions on the electrical impedance. This procedure is proposed as a new tool to face the enormous complexity of the impedance spectroscopy data and is built by following a general but very simple mathematical formulation.

2. Fundamental equations

We consider a system in the Cartesian reference frame with the z-axis perpendicular to the electrodes, located at $z = \pm d/2$. We indicate by N_p and N_m the bulk density of positive (p) and negative (m) particles, respectively. In thermodynamical equilibrium, the material contains a density of N positive and N negative ions, per unit volume, uniformly distributed. It is then supposed to be globally and locally neutral. We assume that the sample is submitted to an external sinusoidal voltage of amplitude V_0 and frequency $f = \omega/2\pi$. Thus, for $V_0 = 0$, we have $N_p(z, t) = N_m(z, t) = N$ and, for $V_0 \neq 0$, it follows that $N_p(z, t) \neq N_m(z, t)$. If we assume furthermore that there is no recombination of ions and that the electrodes are perfectly blocking, the conservation of the number of charges states that $\int_{-d/2}^{d/2} N_p(z, t)\, dz = \int_{-d/2}^{d/2} N_m(z, t)\, dz = Nd$. If, in addition, V_0 is small (linear limit), the actual density of ions differs slightly from N, i.e. if $N_{p,m} = N + n_{p,m}$, it is possible to assume that $n_{p,m} \ll N$. The more general, conventional, framework to face the problem is formed by the PNP models that satisfy Poisson's equation in a finite-length sample, assuming full dissociation of mobile charges of equal mobilities, and, as we will assume here, completely blocking electrodes [15, 23]. This implies that, in the presence of an electric field, of electrical potential V, due to the action of an external power supply or to a charge separation, the bulk densities of this system are obtained by solving the standard form of the continuity equations, namely,

$$\frac{\partial n_p}{\partial t} = -\frac{\partial j_p}{\partial z} \qquad \text{and} \qquad \frac{\partial n_m}{\partial t} = -\frac{\partial j_m}{\partial z}, \qquad (1)$$

in which the densities of currents for positive and negative ions are defined as

$$j_{p,m} = -D_{p,m}\left(\frac{\partial n_{p,m}}{\partial z} \pm \frac{qN}{k_B T}\frac{\partial V}{\partial z}\right), \qquad (2)$$

where $+$ and $-$ stand for positive and negative ions, respectively, q is the electrical charge of the ions, k_B is the Boltzmann constant, and T the absolute temperature. The spatial profile of the electrical potential is governed by Poisson's equation in the form

$$\frac{\partial^2 V(z, t)}{\partial z^2} = -\frac{q}{\varepsilon}[n_p(z, t) - n_m(z, t)], \qquad (3)$$

where ε is the dielectric coefficient of the medium. In the linear limit, we can write $n_{p,m} = \eta_{p,m}e^{i\omega t}$ and $V(z, t) = \phi(z)e^{i\omega t}$. In addition, we assume hereafter that the diffusion coefficients are such that $D_m = D_p = D$. In this way, equation (1) takes the form

$$i\omega\eta_p(z) = D\left[\eta_p''(z) + \frac{qN}{k_B T}\phi''(z)\right], \qquad (4)$$

whereas the Poisson equation, equation (3), becomes

$$\phi''(z) = -\frac{q}{\varepsilon}(\eta_p - \eta_m). \qquad (5)$$

The boundary conditions on $j_{p,m}$ (blocking electrodes, as stated before) are written as

$$j_{p,m}(\pm d/2, t) = 0, \qquad (6)$$

while the ones on the applied potential are simply

$$\phi(\pm d/2) = \pm V_0/2. \qquad (7)$$

This problem has been solved [5, 15, 23–25] and the details of the calculation will be omitted here to save space. The electrical impedance of the cell is given by

$$Z = -i\frac{2}{\omega\varepsilon\beta^2 S}\left\{\frac{1}{\lambda^2\beta}\tanh(\beta d/2) + i\frac{\omega d}{2D}\right\}, \qquad (8)$$

where

$$\beta = \frac{1}{\lambda}\sqrt{1 + i\frac{\omega}{D}\lambda^2}, \qquad (9)$$

and $\lambda = \sqrt{\varepsilon k_B T/(2Nq^2)}$ is the Debye screening length.

The same problem was recently extended by incorporating fractional derivatives on the diffusion equation, equation (1). Bisquert and co-workers [16–19] have analyzed the finite-length Warburg response using fractional derivatives in the time domain. Very recently, finite-length fractional anomalous diffusion (PNPA) models have been proposed and their responses explored [15, 20, 21]. The pure fractional diffusion equation of coefficient γ, such that $0 < \gamma \leq 1$, has been analytically solved together with the Poisson equation to obtain a general expression for equation (8) in the case of one single anomalous diffusion regime [20], i.e. a particular value for γ. A simple derivation for an alternative expression containing a superposition of two regimes (one of which is the usual one, i.e. $\gamma = 1$) can be performed as a particular case of the more general approach dealing with a fractional diffusion equation of distributed order (to be discussed in section 3). To do this, by assuming that the diffusion of ions also presents a fractional component [26], we rewrite equation (1) as a superposition involving a normal diffusive regime and one single anomalous regime characterized by a fractional coefficient γ in the form

$$A\frac{\partial n_p}{\partial t} + B\frac{\partial^\gamma n_p}{\partial t^\gamma} = D\frac{\partial}{\partial z}\left\{\frac{\partial n_p}{\partial z} + \frac{qN}{k_B T}\frac{\partial V}{\partial z}\right\}, \qquad (10)$$

where A is dimensionless, while the dimension of B is $t^{\gamma-1}$. In the linear limit, using equation (10), we get

$$[A(i\omega) + B(i\omega)^\gamma]\eta_p(z) = D[\eta_p''(z) + (qN/k_B T)\phi''(z)], \qquad (11)$$

whereas the Poisson equation does not change. Equation (11) coincides with equation (4) if D is changed in

$$D_e = \frac{D}{A + B(i\omega)^{\gamma-1}}. \qquad (12)$$

In this case, the impedance of the cell is given by

$$Z_e = -i\frac{2}{\omega\varepsilon\beta_e^2 S}\left\{\frac{1}{\lambda^2\beta_e}\tanh(\beta_e d/2) + i\frac{\omega d}{2D_e}\right\}, \qquad (13)$$

where

$$\beta_e = \frac{1}{\lambda}\sqrt{1 + i\frac{\omega}{D_e}\lambda^2}. \qquad (14)$$

To explore the behavior of the impedance in this context, in figure 1, we show the frequency behavior of the real part
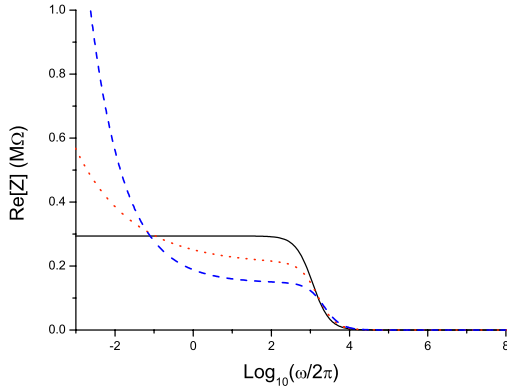
Figure 1. Behavior of the real part of the impedance given by equation (13) for different values of γ: $\gamma = 0.5$ (dashed line), $\gamma = 0.7$ (dotted line), and $\gamma = 1$ (solid line). The curves were drawn for $S = 2 \times 10^{-4}$ m^2, $\varepsilon = 6.7\varepsilon_0$, $d = 25 \times 10^{-6}$ m, $\lambda = 1.076 \times 10^{-7}$ m, and $D = 8.2 \times 10^{-11}$ m^2 s^{-1}.

of Z, as predicted by equation (13) for different values of the fractional coefficient γ. For what concerns the imaginary part, the model predicts that the slopes of the curve in the low frequency region and in the high frequency region are the same (see figure 2).

Two limiting situations should be considered now. The first one is the case $\gamma = 1$ for which $B = 0$ and $A = 1$. In this limit, we recover equation (8). The other limit, which corresponds to a pure fractional case [26], can be obtained by using $A = 0$, and, consequently

$$D_e = \frac{D}{B\,(\mathrm{i}\omega)^{\gamma-1}} \qquad \text{and} \qquad \beta_e = \frac{1}{\lambda}\sqrt{1 + B\frac{(\mathrm{i}\omega)^\gamma \lambda^2}{D}}.$$

In this case, the expression for Z, given by equation (13), becomes

$$Z_e = -\mathrm{i}\frac{2}{\omega\varepsilon\beta_e^2 S}\left\{\frac{1}{\lambda^2\beta_e}\tanh(\beta_e d/2) + B\frac{(\mathrm{i}\omega)^\gamma d}{2D}\right\}, \quad (15)$$

which can be rewritten in the form

$$Z_c = R_c\left[\frac{B\,(\mathrm{i}\omega\tau_c)^{\gamma-1}}{q_c^2} + \frac{\tanh(Mq_c)}{M(\mathrm{i}\omega\tau_c)q_c^3}\right], \quad (16)$$

where $R_c = d\tau_c/(\varepsilon S)$, $M = d/(2\lambda)$, $q_c = \sqrt{1 + B\,(\mathrm{i}\omega\tau_c)^\gamma}$, and $\tau_c = (\lambda^2/D)^{1/\gamma}$. In a very recent paper [21], the predictions of equation (16) were compared with the ones coming from the expression

$$Z_a = R_\infty\{[(\mathrm{i}\omega\tau)^\gamma + \tanh(Mq_a)/Mq_a][(\mathrm{i}\omega\tau)^\gamma(1 + \mathrm{i}\omega\tau)$$
$$+ [(\mathrm{i}\omega\tau) - (\mathrm{i}\omega\tau)^\gamma]\tanh(Mq_a)/Mq_a]^{-1}\}, \quad (17)$$

where, now, $q_a = \sqrt{1 + (\mathrm{i}\omega\tau)^\gamma}$, $\tau = \lambda^2/D = \tau_c^\gamma$, and R_∞ denotes a nondiffusive high frequency limiting resistance that, for complete blocking, is part of an equivalent circuit in which a high frequency limiting capacitance, C_∞, is in parallel with a series combination of an 'interface' impedance, Z_i, and R_∞. Equations (16) and (17) are two distinct, physically plausible empirical generalizations of PNP ordinary diffusion in a cell with plane-parallel electrodes, which reduce exactly to equation (8) in the limit $\gamma \to 1$ [21]. The comparison of these expressions for particular values of the exponent γ showed that equation (17) is not only physically plausible but is also capable of well fitting diverse anomalous diffusion experimental results. On the other hand, a pure fractional expression like the one represented by equation (16), which, as discussed above, is obtained as a particular case of equation (10) when $A = 0$, is not rich enough to face the great complexity represented by the experimental data. Other possibilities, including a model that combines fractional time derivatives with ordinary ones along the lines discussed for equation (10), might lead to physically satisfactory results and might possibly be needed in some situations to best explain experimental data. This generalization is presented and discussed in section 3. Before proceeding, however, in figure 2, the low and high frequency behaviors of the real and imaginary parts of Z, as given by equations (13), (16), and (17) are illustrated for comparative purposes. The curves were drawn for relevant physical parameters, as established by the comparison with experimental data performed in a preceding work [21]. Actual fitting of the data of figure 2 using equation (17) with free parameter values led to results similar to those found when this model was used to fit equation (16) in our comparative work [21], with poor agreement at the lowest frequencies and an estimate of γ very close to unity.
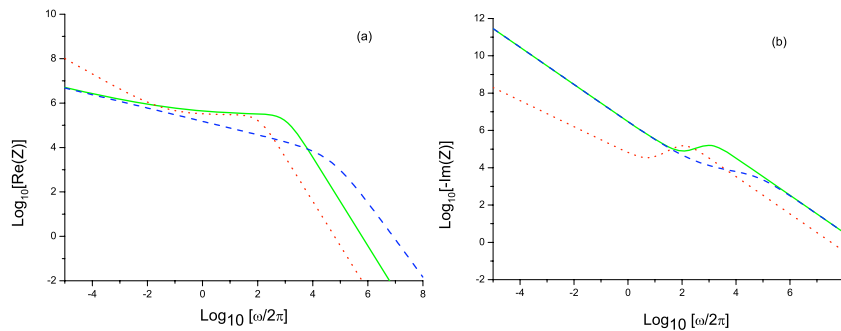

Figure 2. Behavior of the real (a) and imaginary (b) parts of the impedance as predicted by equations (13) (solid line), (16) (dashed line [21]), and (17) (dotted line [21]). The curves were drawn for $\gamma = 0.7$, $\tau = 1.411 \times 10^{-3}$ s, $R_\infty = 2.973 \times 10^5$ Ω, $A = 1$, and $B = 1$. The other parameters are the same as in figure 1.

3. Fractional equation of distributed order

We shall focus our attention on fractional time diffusion equations of distributed orders [27] and investigate the diffusive regimes which can be manifested by them. These equations may be formally written, for example, as

$$\int_0^1 d\bar{\gamma}\, p(\bar{\gamma}) \frac{\partial^{\bar{\gamma}}}{\partial t^{\bar{\gamma}}} n_{\text{p,m}} = -\frac{\partial}{\partial z} j_{\text{p,m}}(z,t), \qquad (18)$$

where $p(\gamma)$ is a distribution function of γ and the operator considered is the Caputo one [28], with $0 < \gamma \leq 1$. It can be defined as

$$\frac{\partial^{\gamma}}{\partial t^{\gamma}} n_{\text{p,m}}(z,t) \equiv {}^{C}_{t_0}D_t^{\gamma}\{n_{\text{p,m}}(z,t)\}$$
$$= \frac{1}{\Gamma(k-\gamma)} \int_{t_0}^{t} d\bar{t}\, \frac{n_{\text{p,m}}^{(k)}(z,\bar{t})}{(t-\bar{t})^{1+\gamma-k}}, \qquad (19)$$

with $k - 1 < \gamma < k$ and $n_{\text{p,m}}^{(k)}(z,\bar{t})$ representing the kth derivative. In particular, we consider $t_0 \to -\infty$ to study the response of the system to the periodic applied potential [28].

Note that equation (18) has the presence of a fractional time operator of distributed order which, depending on the choice of $p(\gamma)$, can account for several diffusive regimes for the ions in the system. In fact, simple cases can be recovered by a suitable choice of $p(\gamma)$. Some examples are the usual one for $p(\bar{\gamma}) = A\delta(\bar{\gamma} - 1)$, the pure fractional case for $p(\bar{\gamma}) = B\delta(\bar{\gamma} - \gamma)$, and the case represented by equation (10), considered in section 2, which is obtained by assuming that $p(\bar{\gamma}) = A\delta(\bar{\gamma} - 1) + B\delta(\bar{\gamma} - \gamma)$. In the preceding expressions, A and B play the role of characteristic times. Since we are considering only mobile positive and negative ions of a single type, with unit valence numbers, the distributed order approach considered here is such that each type of ion can show normal diffusion in one region of time (or frequency) and an anomalous diffusion in another time region. The orders of these derivatives are consequently distributed according to the function $p(\gamma)$, which works as the weight factor for each regime (order).

Thus, the general expression for the impedance is given by [20]

$$Z = -i\frac{2}{\omega \varepsilon \beta^2 S} \left\{ \frac{1}{\lambda^2 \beta} \tanh\left(\frac{\beta d}{2}\right) + \frac{d}{2D} F(i\omega) \right\}, \qquad (20)$$

where, now,

$$\beta = \frac{1}{\lambda} \sqrt{1 + F(i\omega)\frac{\lambda^2}{D}}, \qquad (21)$$

with

$$F(i\omega) = \int_0^1 d\bar{\gamma}\, p(\bar{\gamma})\, (i\omega)^{\bar{\gamma}}. \qquad (22)$$

Notice that the presence of $F(i\omega)$ in equations (20) and (21) is responsible for the incorporation of an arbitrary number of diffusive regimes to the description of the diffusion of ions through the sample. In addition, it is noteworthy that the general expression for the impedance, equation (20), has

exactly the same functional form as equations (8), (13) and (15), which can be faced now in its particular cases.

It is still possible to obtain the same functional form for the impedance if a memory term is present in equation (10). Consider, for instance, the particular case in which $A = 1$ and $B = 0$, i.e. when the fractional time derivative is absent. To account for this memory effect, in this situation, equation (10) could be written in the form

$$\frac{\partial n_{\text{p}}}{\partial t} = D\frac{\partial}{\partial z}\left\{ \frac{\partial n_{\text{p}}}{\partial z} + \frac{qN}{k_B T}\frac{\partial V}{\partial z} \right\} - \int_{-\infty}^{t} dt'\, \alpha(t-t') n_{\text{p}}(z,t'), \qquad (23)$$

where $\alpha(t)$ is the kernel function which quantifies the effect of $n_{\text{p}}(z,t')$ on $n_{\text{p}}(z,t)$. A similar equation is valid for the negative species $n_{\text{n}}(z,t)$. By performing the calculations as in the preceding section, one obtains for the electrical impedance the same expression as equation (13), with β_{e} given again by equation (14), but with a different 'effective' diffusion equation, i.e. equation (12) now becomes

$$D_{\text{e}} = \frac{D}{1 + \bar{\alpha}(i\omega)/i\omega}, \qquad (24)$$

where $\bar{\alpha}(i\omega)$ is the inverse transform of $\alpha(t)$ in the last term of the right-hand side of equation (23). This result illustrates the noteworthy fact that the presence of a general term accounting for some kind of memory effect implies a redefinition of the diffusion coefficient. This redefinition is similar to the one that occurs when fractional time derivatives are considered, as illustrated before in the case of equation (10). Since memory effects can be relevant to explain the diffusion of ions in actual samples, both formalisms presented in this section may eventually be helpful to discuss specific experimental data. In addition, the presence of the kernel $\alpha(t)$ introduces some freedom in the description of the frequency dependence of Z. This liberty in choosing the function $\alpha(t)$ can be useful in a phenomenological perspective of fitting complex experimental data. However, the renormalization of D illustrated in (12) and (24) affects more sensibly the second term of (13) or (20) when the low frequency limit is considered. This seems to indicate that the first term always dictates the low frequency behavior of the real and imaginary parts of Z_{e}.

Even in the general case of many diffusive regimes (i.e. several different values of γ), the system is governed by linear differential equations. For this reason, one expects that for the real, R, and imaginary, X, parts of Z hold the relations of Kramers–Kronig (KK). This is easily demonstrated for the case represented by equation (13). Since the general form of the electrical impedance is preserved, all the properties satisfied by equation (13) are also satisfied by equation (20) whenever the functions $F(i\omega)$ and $\alpha(i\omega)/i\omega$ are analytical functions of ω. For simple superpositions formed from the distribution $p(\gamma)$ considered here or by a suitable choice for $\alpha(i\omega)$, this analyticity is, in principle, always preserved, as will be demonstrated elsewhere.

4. Conclusions

In summary, by using a superposition of anomalous, as well as the usual, diffusive regimes, general expressions for the electrical impedance were analytically obtained. These expressions can be formally obtained by using the so-called fractional diffusion equations of distributed order that combine diffusion equations whose derivatives in the time domain are of arbitrary order in a simple mathematical manner. This combination of fractional time derivatives with ordinary ones may lead to physically satisfactory results and may possibly be needed in some situations to best explain experimental data.

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