Time-Fractional Approach to the Electrochemical Impedance: The Displacement Current

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We establish, in general terms, the conditions to be satisfied by a time-fractional approach formulation of the Poisson-Nernst-Planck model in order to guarantee that the total current across the sample be solenoidal, as required by the Maxwell equation. Only in this case the electric impedance of a cell can be determined as the ratio between the applied difference of potential and the current across the cell. We show that in the case of anomalous diffusion, the model predicts for the electric impedance of the cell a constant phase element behaviour in the low frequency region. In the parametric curve of the reactance versus the resistance, the slope coincides with the order of the fractional time derivative.

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The Poisson-Nernst-Planck (PNP) diffusional model is formulated to consider a neutral species that can dissociate into positive and negative charges of arbitrary mobilities \cite{1, 2}. In the presence of the external electric field $E(r,t)$, these charges move, giving rise to currents of neutral as well as of positive and negative charges. If we denote the bulk density of these particles, respectively with $n_n(r,t)$, $n_p(r,t)$, and $n_m(r,t)$ and, likewise, the current density as $j_n(r,t)$, $j_p(r,t)$, and $j_m(r,t)$, the continuity equations will be written as

$$\frac{\partial}{\partial t} n_n(r,t) = -\nabla \cdot j_p(r,t) + S(r,t),$$
$$\frac{\partial}{\partial t} n_p(r,t) = -\nabla \cdot j_n(r,t) + S(r,t),$$
$$\frac{\partial}{\partial t} n_m(r,t) = -\nabla \cdot j_m(r,t) - S(r,t),$$

where $S(r,t)$ accounts for a source term related to the dissociation of neutral particles and recombination of the ions. In the case of a full dissociation the neutral particles disappear, as well as the source term. To obtain the set of fundamental equations of the PNP model, we have to consider also the Poisson equation, written as

$$\nabla \cdot E(r,t) = \frac{q}{\varepsilon} [n_p(r,t) - n_m(r,t)],$$

where $\varepsilon$ is the dielectric permittivity of the insulating medium free of ions. This equation connects the bulk density of ions of positive and negative charges, of absolute value $q$, to the actual profile of the electric field across the sample.

The total electric current is formed by the conduction and the displacement currents:

$$j(r,t) = q \left[ j_p(r,t) - j_m(r,t) \right] + \varepsilon \frac{\partial E(r,t)}{\partial t}. \quad (3)$$

If we now combine the first two of Eqs. (1) with Eq. (3), we conclude that

$$\nabla \cdot j = -q \left\{ \frac{\partial}{\partial t} [n_p(r,t) - n_m(r,t)] \right\} + \varepsilon \nabla \cdot \frac{\partial E(r,t)}{\partial t} = 0,$$

when the equation of Poisson, Eq. (2), is used. Indeed, the total current has to be solenoidal, i.e.,

$$\nabla \cdot j(r,t) = \nabla \cdot \left\{ q \left[ j_p(r,t) - j_m(r,t) \right] + \varepsilon \frac{\partial E(r,t)}{\partial t} \right\} = 0.$$

In this case, for a one-dimensional problem, the current density $j$ is position independent. Only in this framework, the concept of electrical impedance, defined as the ratio between the difference of potential applied to the system and the total electric current flowing across it, is meaningful \cite{3}. To proceed with the application of the PNP model to deal with experimental data obtained in electrolytic cells, the set of Eqs. (1) and (2) has to be solved for well-defined boundary conditions. Anyway, the total current flowing though the cell is subjected to the general condition established in Eq. (5), i.e., the total current has to be solenoidal.

Perhaps the simplest extension of the problem using derivatives operators of arbitrary order, commonly called fractional derivatives, should read as the one we have

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proposed some years ago [4]:

\[
\tau^{-1} \partial_t^n n_p(r,t) = -\nabla \cdot j_p(r,t) + S(r,t),
\]

\[
\tau^{-1} \partial_t^n n_m(r,t) = -\nabla \cdot j_m(r,t) + S(r,t),
\]

\[
\tau^{-1} \partial_t^n n_d(r,t) = -\nabla \cdot j_d(r,t) - S(r,t),
\]

where \( \tau \) is an intrinsic time of the problem. In Eqs. (9) we have replaced the time derivative present in Eqs. (1) with the Riemann-Liouville fractional derivative, by promoting the change:

\[
\frac{\partial n_{p,m}(r,t)}{\partial t} \rightarrow \frac{\partial^n n_{p,m}(r,t)}{\partial t^n} \rightarrow t_0 D_t^n n_{p,m}(r,t),
\]

and used the definition of the Riemann-Liouville operator as

\[
t_0 D_t^n n_{p,m}(r,t) = \frac{1}{\Gamma (m - \gamma)} \frac{d}{dt} \int_{t_0}^{t} \frac{d^n n_{p,m}(r,\tau)}{(t-\tau)^{\gamma+1-m}}.
\]

where \( m - 1 < \gamma < m \), with \( m \) an integer, and \( t_0 \) is related to the conditions initially imposed to the system. For an analysis of the kind we are proposing here, focused on the impedance spectroscopy, without loss of generality we can consider \( t_0 = -\infty \) to study the response of the system to the periodic applied potential, as required by the impedance spectroscopy technique. If we now combine the new set of fundamental equations of the extended model, which are Eqs. (6) and (2), following the procedure used before, it is mandatory to conclude that \( \nabla \cdot j(r,t) = 0 \), i.e.,

\[
\nabla \cdot \left\{ q [j_p(r,t) - j_m(r,t)] + \varepsilon \tau^{-1} \frac{\partial^n E(r,t)}{\partial t^n} \right\} = 0.
\]

This means that a physically sound extension of the PNP model using fractional derivatives requires an extended expression in which the displacement current is also defined in terms of a derivative of arbitrary order. This fact has profound implications and requires discussing also possible extensions of the Maxwell equations to the field of the differential operators of arbitrary order. Before analyzing this important aspect of the problem, to keep the approach as general as possible, let us consider a further step in the generalization of the PNP model using the time-fractional derivative.

One possible way to generalize the previous equations is to use the so-called time-fractional derivative operator of distributed order, defined as [3, 4]:

\[
\int_{-\infty}^{1} d\gamma p(\gamma) -\infty D_t^\gamma (\cdots),
\]

where \( p(\gamma) \) is a distribution of \( \gamma \), with \( \int_{0}^{1} d\gamma p(\gamma) = 1 \), instead of using only a single fractional operator \( -\infty D_t^{\gamma} (\cdots) \). After implementing this generalization, the set of fundamental equations of the extended PNP model will be now formed by the following continuity equations:

\[
\int_{0}^{1} d\gamma p(\gamma) \tau^{-1} \frac{\partial^n n_p(r,t)}{\partial t^n} = -\nabla \cdot j_p(r,t) + S(r,t),
\]

\[
\int_{0}^{1} d\gamma p(\gamma) \tau^{-1} \frac{\partial^n n_m(r,t)}{\partial t^n} = -\nabla \cdot j_m(r,t) + S(r,t),
\]

\[
\int_{0}^{1} d\gamma p(\gamma) \tau^{-1} \frac{\partial^n n_d(r,t)}{\partial t^n} = -\nabla \cdot j_d(r,t) - S(r,t),
\]

and the equation of Poisson, Eq. (2). Combining again, as before, these equations, it is possible to show that

\[
\int_{0}^{1} d\gamma p(\gamma) \tau^{-1} \frac{\partial^n [n_p(r,t) - n_m(r,t) - n_d(r,t)]}{\partial t^n} \nabla \cdot [j_p(r,t) - j_m(r,t) - j_d(r,t)] = 0,
\]

and, consequently, that

\[
\nabla \cdot \left\{ q [j_p(r,t) - j_m(r,t)] + \varepsilon \int_{0}^{1} d\gamma p(\gamma) \tau^{-1} \frac{\partial^n E(r,t)}{\partial t^n} \right\} = 0.
\]

Equation (13) is now more general than Eq. (9) and implies that the total electric current

\[
j(r,t) = q [j_p(r,t) - j_m(r,t)]
\]

\[
+ \varepsilon \int_{0}^{1} d\gamma p(\gamma) \tau^{-1} \frac{\partial^n E(r,t)}{\partial t^n}
\]

is solenoidal, as in the previous cases. If we consider \( p(\gamma) = \delta(\gamma - 1) \), then Eqs. (11) reduce to Eqs. (1), as well as Eq. (13) reduces to Eq. (6). Other forms of \( p(\gamma) \) may express a superposition of different diffusive regimes. For instance, \( p(\gamma) = A \delta(\gamma - 1) + B \delta(\gamma - \alpha) \), where \( A \) and \( B \) are connected with characteristic times, represents a superposition of a normal diffusion equation (\( \gamma = 1 \)) with a diffusion equation of arbitrary order \( \gamma = \alpha \), with \( 0 < \alpha \leq 1 \).

In the prototypical case of time-fractional derivative of order \( \gamma \), as in Eq. (9), the displacement current assumes the form:

\[
j_D(r,t) = \varepsilon \tau^{-\gamma-1} \frac{\partial^n E(r,t)}{\partial t^n}.
\]

For consistency, the definition of a modified displacement current in terms of a fractional time-derivative operator requires an appropriated formulation of a time-fractional electrodynamics, which, needless to say, is a hard task. Recently, some approaches have been presented to deal with these kinds of formulation. Analog for Maxwell’s equations using time-fractional derivatives in the Riemann-Liouville and Caputo sense have been obtained by introducing time integro-differentiation of arbitrary order into the fundamental equations of the electrodynamics of a material media [7]. The analysis shows that the stochastic nature of charged particles motion in a medium, properly described in terms of fractional operators, influences the dynamics of an electromagnetic field.
More recently, a formulation of time-fractional electrodynamics was derived based on the Riemann-Silberstein vector \([9]\). The use of this vector together with fractional-order derivatives indicates a way to write Maxwell’s equations in terms of time-fractional derivatives in a compact form, which allows for modeling of energy dissipation and dynamics of electromagnetic systems with memory. These generalizing approaches require a displacement current exactly in the form we are proposing here. They open the possibility to interpret the displacement currents, arising in the formulation of the time-fractional PNP model, in the appropriate electrodynamics’s framework.

The PNP model is a very useful framework to interpret impedance spectroscopy data regarding a wide variety of systems and electrolytes. In the range of frequency for which it works particularly well in describing the presence of the ions in the sample to the stimulus of an external field, the electric current used to determine the electric impedance of the cell has to include the displacement current related to the time variation of the electric field. If the diffusion is normal, it is given by \( j = \varepsilon \beta D \Delta \varepsilon \partial^\gamma E / \partial t^\gamma \). If the diffusion is anomalous it is given by \( j = \varepsilon \beta D \Delta \varepsilon \partial^\gamma E / \partial t^\gamma + \varepsilon \Phi(\omega) \beta D \Delta \varepsilon \partial^\gamma (\varepsilon \beta D) / \partial t^\gamma \). The important point is that, in the framework of anomalous diffusion the displacement current cannot be used in its usual, i.e., non-fractional form. To analyze this aspect of the problem in more detail, let us consider a typical problem dealing with the impedance of an electrolytic cell. The proper application of the technique requires an electric field in the form:

\[
E(r, t) = F(r)e^{i\omega t},
\]

where \( \omega = 2\pi f \) is the circular frequency of the applied field. From Eqs. [15] and [16], and again using the equation of Poisson, Eq. [2], we may write

\[
\nabla \cdot j = -\varepsilon \nabla \cdot \left[ \tau^{\gamma - 1} \frac{\partial^\gamma E(r, t)}{\partial t^\gamma} - \frac{\partial E(r, t)}{\partial t} \right].
\]

Now, if we use the definition of the electric field as in Eq. [16], we obtain:

\[
\nabla \cdot j = -\varepsilon (\nabla \cdot F)(i\omega) [(i\tau\omega)^{\gamma - 1} - 1],
\]

which is solenoidal only if \( \gamma = 1 \). However, if the difference \( (i\tau\omega)^{\gamma - 1} \) may be considered negligible, the requirement of solenoidal current flowing through the system is essentially fulfilled, and the time-fractional approach to the PNP model may be fruitfully employed to analyze experimental data of impedance spectroscopy, as done in the last decades [9]. Some special attention has to be devoted to the \( \omega \to 0 \) limit, since \( 0 \leq \gamma \leq 1 \). Consequently the condition on the solenoidal character of \( j \) is violated in the dc limit.

In addition, when this condition is satisfied, a connection between the impedance spectroscopy response of an anomalous Poisson-Nernst-Planck (PNP) diffusional model and of equivalent circuits containing constant phase elements (CPEs) may be established in general terms for a typical electrolytic cell \([10]\).
The other term present in Eq. (22) is absent in Eq. (23) for the imaginary part of the impedance in the very low frequency limit. The first addendum in Eq. (22) is directly related to the resistance of the cell, it is a bulk contribution and it scales with the thickness of the cell, \( d \). The other term depends on frequency, contributing to the real and imaginary parts of the impedance in the low frequency limit.

This can be checked by considering in more detail the asymptotic behavior of the impedance in the low frequency limit, which, for Eq. (21), is given by

\[
Z \approx \frac{\lambda^2 d}{\varepsilon AD} \Phi(i\omega) + 2\lambda \frac{1}{\varepsilon A} \Phi(i\omega). \tag{22}
\]

The first addendum in Eq. (22) is directly related to the resistance of the cell, it is a bulk contribution and it scales with the thickness of the cell, \( d \). The other term depends on frequency, contributing to the real and imaginary parts of the impedance in the low frequency limit.

\[
Z \approx \frac{\lambda^2 d}{i\omega\varepsilon AD} \Phi(i\omega) + 2\lambda \frac{1}{i\omega\varepsilon A}, \tag{23}
\]

with a different behavior for the impedance. In particular, the behavior related to the constant phase element present in Eq. (22) is absent in Eq. (23) for the imaginary part of the impedance in the very low frequency limit.

To sum up, we have analyzed the role of the displacement current in a generalized time-fractional approach to the PNP model for electrical impedance. We have shown that, in order to keep the concept of electrical impedance meaningful, the total electric current arising in this extended model has to be solenoidal. This requirement implies that also the expression of the displacement current has to be modified by extending it to the fractional domain too. The proposed form of the displacement current coincides with the one used recently in some generalizations of the Maxwell equations for material media involving fractional order operators. The time-fractional extension of PNP model naturally exhibits a CPE-like
behavior of the electrical impedance in the low frequency region of the spectra and is shown to be a powerful tool to face a wide variety of complex behaviour found in electrolytic cells. From the analysis reported above, we conclude that the CPE behaviour observed in the frequency dependence of the impedance of electrolytic systems, can have different origin [13]. However, in the case of media presenting a porous structure, it could be related to the anomalous diffusion of the ions in it.

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