

Fractional Diffusion Equation and Impedance Spectroscopy of Electrolytic Cells

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Received: May 20, 2009; Revised Manuscript Received: July 8, 2009

The influence of the ions on the electrochemical impedance of a cell is calculated in the framework of a complete model in which the fractional drift-diffusion problem is analytically solved. The resulting distribution of the electric field inside the sample is determined by solving Poisson's equation. The theoretical model to determine the electrical impedance we are proposing here is based on the fractional derivative of distributed order on the diffusion equation. We argue that this is the more convenient and physically significant approach to account for the enormous variety of the diffusive regimes in a real cell. The frequency dependence of the real and imaginary parts of the impedance are shown to be very similar to the ones experimentally obtained in a large variety of electrolytic samples.

The electrochemical impedance technique is used to investigate electrical properties of liquid materials.¹ The sample is submitted to an ac voltage of small amplitude to ensure that its response to the external signal is linear. Then, the impedance, Z , is measured as a function of the frequency $\omega/2\pi$ of the applied voltage.² In the low frequency region, of particular importance is the role of the ions on the value of the measured impedance because they contribute to the electrical current. In this frequency region, the theoretical analysis of the influence of the ions on the electrical impedance is performed by solving the continuity equations for the positive and negative ions and the Poisson equation for the actual electric potential across the sample. The standard analysis predicts that the real part of the electrical impedance is frequency independent up to the relaxation frequency, whereas the imaginary part in the dc limit diverges as $1/\omega$. However, the experimental data are not in agreement with these predictions. For this reason, several models have been proposed to account for the observed effect of the ions on the electrical response of the cell.³ It seems to be out of doubt that the adsorption phenomena has a central role.² This should be the first and main mechanism. However, the adsorption alone is not able to account for the experimental features found in these systems. Therefore, also the role of nonblocking electrodes has been invoked to shed some light on the problem. In some sense, both situations should also be analyzed by considering the adsorption process in which memory effects could play some role.^{4,5} In this case, the kinetic equation at the interface incorporates memory effects in the process by means of three different kernels, whose importance is associated with the predominance of chemisorption or physisorption in the adsorption-desorption processes.⁴ The net result is that the density of adsorbed particles at the surface can present oscillations with time before reaching a stationary regime.^{4,5} Another mechanism could be connected with the accumulation of ions near the

surface, in the absence of adsorption phenomena. This accumulation should be connected with the necessity to modify Fick's law and to solve a modified diffusion equation. In this direction, the fractional diffusion equation can be the theoretical framework to take into account this effect on the impedance. Recently, Bisquert and co-workers^{6–9} have investigated several models to address the electrochemical impedance of diffusion by means of fractional calculus. In these pioneering works, the impedance at high frequency was shown to behave as $Z \propto (i\omega)^{-\gamma/2}$, and, at low frequency, as $Z \propto (i\omega)^{-\gamma}$, where γ is the fractional coefficient. These results are a first generalization in the framework of fractional calculus for the behavior of Warburg impedance¹⁰ (high frequency) and for the predictions of the constant phase element (CPE) impedance model (low frequency). However, in these approaches, the effective electric field inside the sample is taken as the applied external field; i.e., no spatial distribution of charges is determined. This means that the influence of the ions on the spectroscopy impedance measurements is not taken into account in a complete manner.

In this Letter, we use a different strategy and solve the complete problem; i.e., we consider the presence of the drift term coupled with the Poisson equation. This step is essential to incorporate the contribution of the ions, present in the sample, to the correct spatial distribution of the electric field. In the present approach, a fractional diffusion equation is exactly solved by means of integral transformation techniques and the final impedance of the cell is analytically determined in the absence of the adsorption phenomena. The frequency dependence of the real and imaginary parts of the impedance are obtained in terms of closed analytical expressions. As a step further, we consider also the general case of fractional derivatives of distributed order to incorporate the possibility of different diffusive regimes in the sample. When this formalism is invoked on the diffusion equation, we achieve a complete description of the phenomenon which gives the usual result in the appropriated limit but also predicts new and rich behavior,

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qualitatively very similar to the ones presented in real systems for the entire range of frequencies and not explained until now.

A simple model to take into account for the effect of the accumulated ions considers a cell in the shape of a slab of thickness d , limited by two flat surfaces placed in $z = \pm d/2$. This cell is filled with an isotropic liquid, inside which dimensionless ions (positive, with density n_+ and negative, with density n_-) are dispersed, forming a homogeneous medium of dielectric constant ϵ . The surfaces are supposed as nonadsorbing, the monovalent ions, of charge q , are supposed to have the same mobility $\mu_+ = \mu_-$, and, before the application of an external field, the liquid is locally and globally neutral. When the external field is turned on, the liquid becomes locally charged but remains globally neutral. For the investigations connected with the impedance spectroscopy, the sample is submitted to an external sinusoidal voltage of amplitude V_0 and frequency $f = \omega/2\pi$ and the surfaces are prepared to work as blocking electrodes. In this case, for $V_0 = 0$, $n_+(z,t) = n_-(z,t) = N$ and, if we neglect recombination of ions, we have $\int_{-d/2}^{d/2} n_+(z,t) dz = \int_{-d/2}^{d/2} n_-(z,t) dz = Nd$, stating the conservation of the number of particles. If, on the other hand, $V_0 \neq 0$, $n_+(z,t) = n_-(-z,t)$. We write $n_+(z,t) = N + \delta n_+(z,t)$ and $n_-(z,t) = N + \delta n_-(z,t)$, where δn_{\pm} represents the bulk density of ions due to the presence of the external field. From the hypothesis of global neutrality, we have $\int_{-d/2}^{d/2} \delta n_+(z,t) dz = \int_{-d/2}^{d/2} \delta n_-(z,t) dz = 0$. Under these assumptions, the problem to obtain the current flowing through the cell can be solved by considering the three fundamental equations of the problem. These are the continuity equations

$$\frac{\partial}{\partial t} \delta n_{\pm}(z,t) = -\frac{\partial}{\partial z} j_{\pm}(z,t) \quad (1)$$

where the density of currents for positive and negative ions are

$$j_{\pm}(z,t) = -\mathcal{K} \left(\frac{\partial}{\partial z} \delta n_{\pm}(z,t) \pm \frac{Nq}{k_B T} \frac{\partial}{\partial z} V(z,t) \right) \quad (2)$$

where k_B is the Boltzmann constant, T is the absolute temperature, and \mathcal{K} is the diffusion coefficient, and the Poisson equation

$$\frac{\partial^2}{\partial z^2} V(z,t) = -\frac{q}{\epsilon} (\delta n_+(z,t) - \delta n_-(z,t)) \quad (3)$$

Equation 2 holds in the limit for which $|\delta n_{\pm}| \ll N$, which is always true if the amplitude of the external voltage is low enough. Only in this framework the concept of electrical impedance is meaningful because the system behaves in a linear manner (eqs 1 and 3 are linear). These equations have to be solved with the imposed boundary conditions on $j_{\pm}(z,t)$, i.e., $j_{\pm}(\pm d/2,t) = 0$, and on the difference of potential $V(z,t)$: $V(\pm d/2,t) = \pm(V_0/2)e^{i\omega t}$. This problem has been solved in detail and is extensively discussed in ref 2.

Now, let us consider an extension of the problem discussed above by incorporating fractional time derivatives on the diffusion equation which emerges from eqs 1 and 2, leading us to a fractional diffusion equation. Notice that the fractional diffusion equations^{11–13} have been used to investigate several scenarios related to anomalous diffusion such as chaotic systems,¹⁴ diffusion on fractals,¹⁵ subdiffusion in a membrane,¹⁶ DNA translocation,¹⁷ time-dependent external field on subdiffusing particles,¹⁸ Brownian motion in a double well potential,¹⁹

and in the description of anomalous dielectric relaxation in the context of the Debye model.^{20–23} Following the procedure employed by Bisquert and co-workers,^{6–9} which has obtained useful results for impedance, we extend the time derivative present in eq 1 to the Riemann–Liouville fractional derivative:²⁴

$${}_t^{\gamma} \mathcal{D}_t^{\gamma} \delta n_{\pm}(z,t) = \frac{1}{\Gamma(m-\gamma)} \frac{d^m}{dt^m} \int_{t_0}^t d\bar{t} \frac{\delta n_{\pm}(z,\bar{t})}{(t-\bar{t})^{\gamma+1-m}} \quad (4)$$

where $m-1 < \gamma < m$ and t_0 is related to the conditions initially imposed on the system. In particular, we consider $t_0 = -\infty$ to study the response of the system to the periodic applied potential defined above, as indicated by ref 24. Substituting eq 1 into eq 2 and taking these conditions into account, we obtain

$$-{}_{-\infty}^{\gamma} \mathcal{D}_t^{\gamma} \delta n_{\pm}(z,t) = \mathcal{K}_{\gamma} \frac{\partial^2}{\partial z^2} \delta n_{\pm}(z,t) \pm \frac{Nq\mathcal{K}_{\gamma}}{k_B T} \frac{\partial^2}{\partial z^2} V(z,t) \quad (5)$$

where \mathcal{K}_{γ} represents the diffusion coefficient and the second term results from the drift term with the assumption that $|\delta n_{\pm}| \ll N$, as discussed before. In this way, we analyze the system in the presence of a drift and simultaneously subjected to diffusion and Poisson's equation as a consequence of the presence of ions. We note that the framework used here is different from the one presented in refs 7–9 and 25 because the spatial distribution of the electric field inside the sample is determined.

To proceed further with the investigation of the role of the ions on the impedance spectroscopy by means of a fractional approach, we have to obtain the total current in the external circuit, taking into account the presence of the ions. This means that we have to solve eq 5 accomplishing eq 3, considering the current density in the form of eq 2 with \mathcal{K} substituted with \mathcal{K}_{γ} . We assume that $V(z,t) = v(z)e^{i\omega t}$ and $\delta n_{\pm}(z,t) = \rho_{\pm}(z)e^{i\omega t}$. By substituting the proposed solution in eq 5, we obtain the following equations:

$$\rho_{\pm}''(z) - \frac{1}{\lambda_1^2} \rho_{\pm}(z) + \frac{1}{2\lambda_D^2} \rho_{\mp}(z) = 0 \quad (6)$$

with

$$\frac{1}{\lambda_1^2} = \frac{1}{2\lambda_D^2} + \frac{(i\omega)^{\gamma}}{\mathcal{K}_{\gamma}} \text{ and } \lambda_D = \sqrt{\frac{k_B \epsilon T}{2Nq^2}} \quad (7)$$

where λ_D is the Debye screening length. Note that, to obtain the above system of equations, we have used the result ${}_{-\infty}^{\gamma} \mathcal{D}_t^{\gamma}(e^{i\omega t}) = \lambda^{\gamma} e^{i\omega t}$ presented in ref 24 for $0 < \gamma \leq 1$ by replacing λ by $i\omega$. This system of differential equations obtained for ρ_+ and ρ_- may be solved by employing $\rho_{\pm}(z) = \mathcal{C}_{\pm} e^{\nu z}$, leading us to a system of equations:

$$\nu^2 \mathcal{C}_{\pm} - \frac{1}{\lambda_1^2} \mathcal{C}_{\pm} + \frac{1}{2\lambda_D^2} \mathcal{C}_{\mp} = 0 \quad (8)$$

for which nontrivial solutions exist only if

$$v_{1,2} = \pm\beta = \pm\sqrt{\frac{1}{\lambda_D^2} + \frac{(i\omega)^\gamma}{\mathcal{K}_\gamma}} \text{ and } v_{3,4} = \pm\sqrt{\frac{(i\omega)^\gamma}{\mathcal{K}_\gamma}} \quad (9)$$

which are the characteristic exponents of the problem. In comparison with the results of ref 2, these exponents incorporated a dependence on the fractional coefficient γ and are reduced to the ones previously determined when $\gamma \rightarrow 1$. The rest of the calculation is performed in a way very similar to the one developed in ref 2 and will be omitted to save space. In this manner, the impedance will be given by $Z = V_0/(i\omega\epsilon v'(d/2)S)$, where S is the surface area of the electrodes. By using the results obtained above, we can write the impedance in the form

$$Z = \frac{2}{i\omega\epsilon S\beta^2} \left[\frac{1}{\lambda_D^2\beta} \tanh\left(\frac{\beta d}{2}\right) + \frac{(i\omega)^\gamma d}{2\mathcal{K}_\gamma} \right] \quad (10)$$

This formula is very similar to eq 11.40 of ref 2. The important difference is again the fractional coefficient γ . The usual results are recovered in the limit $\gamma \rightarrow 1$.

In Figure 1, $\text{Re}(Z)$, as calculated by eq 10, is shown as a function of the frequency for typical values of material parameters in an electrolytic cell. The value $\gamma = 1.0$, shown with a dotted line, is depicted for comparative purposes because it represents the normal diffusive behavior. The deviations from this normal behavior are remarkable and more pronounced for decreasing values of γ . In Figure 2, $\text{Im}(Z)$, as calculated by eq 10, is also shown. In this case, the main differences are obtained for decreasing values of γ in the high frequency region.

The diffusion phenomenon that happens near the interface is very complicated and involves several mechanisms. Furthermore, since the surfaces are not homogeneous, the diffusion has different characteristics at different points in the sample. In this manner, a generalization of our analysis according to the lines suggested in refs 28–31 can be useful to analyze the experimental data. More precisely, the previous results, obtained for the impedance in the framework of the fractional diffusion eq 5, may also be extended further by considering the fractional diffusion equations of distributed order.^{28–31} A possible generalization suggests to consider $\int_0^1 d\bar{\gamma} p(\bar{\gamma}) {}_{-\infty}\mathcal{D}_t^{\bar{\gamma}}(\dots)$, where $p(\bar{\gamma})$ is a distribution of $\bar{\gamma}$ with $\int_0^1 d\bar{\gamma} p(\bar{\gamma}) = 1$, instead of the fractional operator ${}_{-\infty}\mathcal{D}_t^{\bar{\gamma}}(\dots)$. For this case, the impedance is formally given by eq 10 with $(i\omega)^\gamma \rightarrow \int_0^1 d\bar{\gamma} p(\bar{\gamma})(i\omega)^{\bar{\gamma}}$. The same change needs to be performed for the quantity β presented in eq 10. A remarkable point about the fractional derivative of distributed order on the diffusion equation is the presence of different diffusive regimes.³¹ In fact, this characteristic is manifested by the quantities obtained from these equations, in particular the impedance. The physical insight one gains from this analysis can be better appreciated if one considers that $\gamma = 1$ represents the normal diffusion process, while $\gamma < 1$ represents a subdiffusive process. When two typical situations of this kind can be considered in a unique approach, one achieves a more complete phenomenological description of complex phenomena without having to deal with a large number of free parameters. For illustrative purposes, we consider the case $p(\bar{\gamma}) = 1/5\delta(\bar{\gamma} - 1/2) + 4/5\delta(\bar{\gamma} - 1)$, which yields

$$\beta = \pm\sqrt{\frac{1}{\lambda_D^2} + \frac{1}{5}\frac{(i\omega)^\gamma}{\mathcal{K}_\gamma} + \frac{4}{5}\frac{i\omega}{\mathcal{K}_\gamma}} \quad (11)$$

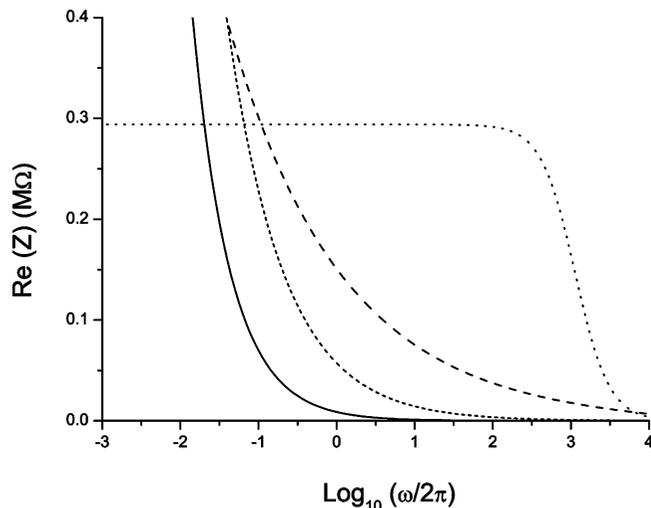


Figure 1. Real part of the impedance of the cell vs the frequency for the set of parameters: $\epsilon = 6.7\epsilon_0$ (where ϵ_0 is the dielectric permittivity of the free space); $N = 4 \times 10^{20} \text{ m}^{-3}$, $\mathcal{K} \approx 8.2 \times 10^{-12} \text{ m}^2/\text{s}$,^{26,27} $d = 25 \text{ }\mu\text{m}$, and $S = 2 \times 10^{-4} \text{ m}^2$. With these values, $\lambda_D \approx 10^{-7} \text{ m}$. The curves were drawn for $\gamma = 0.1$ (solid), $\gamma = 0.4$ (short dash), $\gamma = 0.7$ (dash), and $\gamma = 1.0$ (dot).

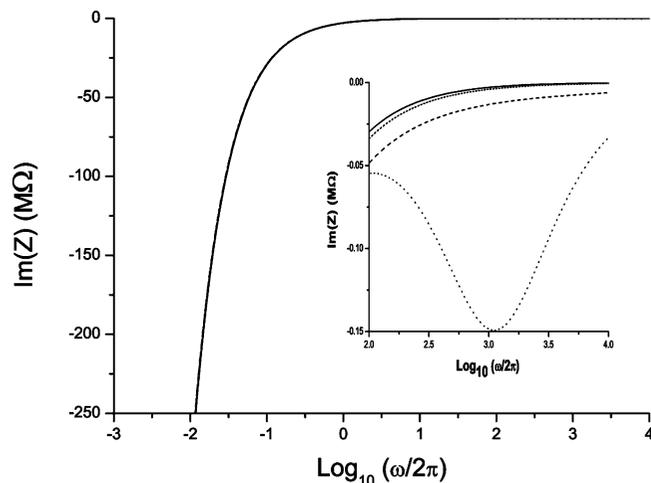


Figure 2. Imaginary part of the impedance of the cell vs the frequency for the same set of parameters and for the same values of γ shown in Figure 1. The inset refers to high values of ω .

In Figure 3, $\text{Re}(Z)$, calculated by eq 10 with the modifications presented above, is shown again for the same set of parameters of Figures 1 and 2. The existence of a plateau for small values of γ is evident (e.g., $\gamma = 0.1$, as shown in the figure). Moreover, the illustrative curves show that the low frequency behavior of $\text{Re}(Z)$ is strongly influenced by the anomalous diffusive regime, i.e., the values of $\gamma < 1$, whereas the high frequency behavior is essentially the same as the one predicted by the normal diffusive behavior $\gamma = 1$. In Figure 4, $\text{Im}(Z)$ is shown as a function of the frequency. Again, one observes that the variations in the diffusive regime are sensible only in the case of high values of the frequency, as shown by the inset in this figure. The frequency dependences of $\text{Re}(Z)$ and $\text{Im}(Z)$ are similar to the ones experimentally observed in electrolytes and are usually interpreted in terms of the CPE impedance model.^{25,32,33}

To sum up, we have presented a complete approach to determine the impedance of an electrolytic cell when the phenomenon of the anomalous diffusion is taken into account. The presented framework is complete in the following sense. The diffusion equation, with a drift term, is solved at the same time in which the influence of the ions present in the sample is

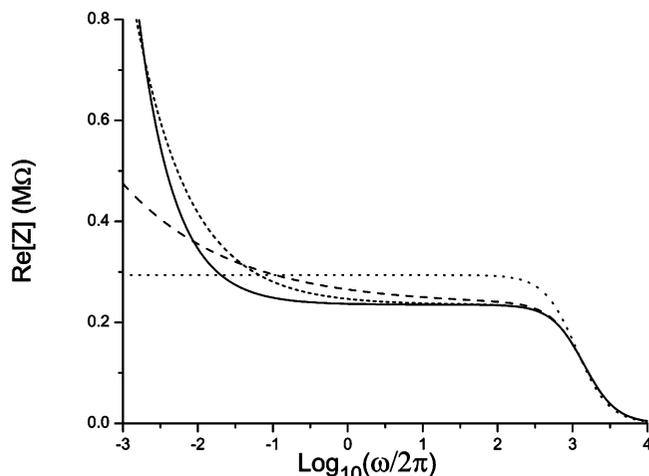


Figure 3. Real part of the impedance of the cell vs the frequency for the same set of parameters and for the same values of γ shown in Figure 1.

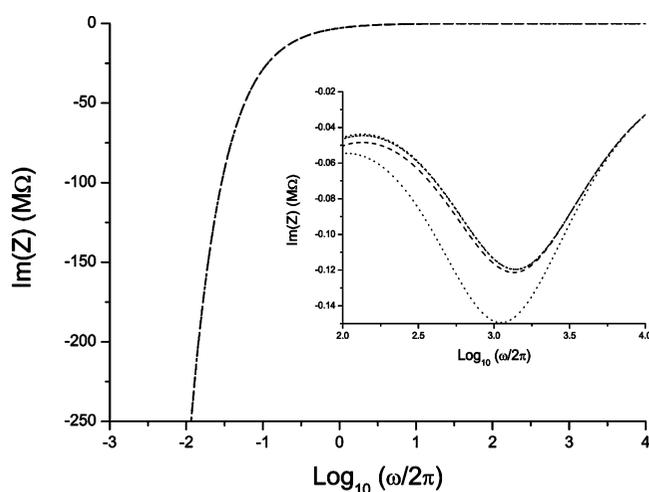


Figure 4. Imaginary part of the impedance of the cell vs the frequency for the same set of parameters and for the same values of γ shown in Figure 3. The inset refers to high values of ω .

considered by means of the Poisson equation. Furthermore, the diffusive process is considered in a general formalism represented first by the fractional diffusion equation for which anomalous diffusion (subdiffusive regime) can be found. This means that the diffusion of the ions follows a nonconventional behavior in the sample. As a consequence, the behavior of $\text{Re}(Z)$ and $\text{Im}(Z)$ as a function of the frequency are strongly dependent on the fractional index, i.e., on the kind of diffusive regime. This long lasting memory behavior, which in some sense arises in this context, may be a consequence of the conservation of the number of particles imposed on the system to correctly account for the interfacial behavior.³⁴ After that, we extend this approach by considering the fractional derivative of distributed order on the diffusion equation. The results obtained in this case are close to the results obtained in real systems both for high and low frequency. The framework we are proposing reveals itself the correct one to face all the complexities of the diffusive behavior of an electrolytic cell. As a matter of fact, our results

indicate that, to correctly describe the frequency behavior of a given cell, the fractional diffusion equation is the more convenient framework. More specifically, only when the fractional derivative of distributed order is invoked on the diffusion equation, we achieve a complete description of the phenomenon. This means that the diffusive process that takes place inside the sample is not characterized by a unique regime. It is multifaced and is better described when one considers the presence of different, normal as well as anomalous, diffusion regimes for the ions inside the cell.

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