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Insight on the surface polarisation for non-blocking electrodes

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A complete phenomenological description of the electrode polarisation and of the non-blocking character of electrodes is theoretically discussed. To do this, the role of the ions on the electrical response of an electrolytic cell submitted to an external field of small amplitude is investigated. We assume that the conduction current across the electrodes is limited by energy barriers which determine the activation energy of the corresponding electrochemical reactions responsible for the processes of charge transfer between the solution containing ions and the external circuit. This assumption implies that the boundary conditions for the conduction current on the electrodes contain two terms: one proportional to the surface electric field, as in the Ohmic model, and the other proportional to the surface variation of the bulk concentration of ions, as in the Chang-Jaffe model. We deduce, in the one-mobile ion approximation, the expression for the electric impedance of the cell, in the shape of a slab, for mixed boundary conditions. Our expression contains, as particular cases, the Ohmic and Chang-Jaffe models. The equivalence between the general case considered in our analysis and previous models is discussed. © 2016 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4943171>]

I. INTRODUCTION

The electrode polarization in an electrolytic cell is due to the accumulation of the ions present in the electrolytic solution when the cell is submitted to an external electric field. The formation of two charged surface layers strongly influences the electric response of the electrolytic cell when an external electric field periodic in time is applied. Even if the medium in which the ions are present is not dispersive, the ions are responsible for a typical dielectric dispersion in the frequency range up to a few MHz.

A used approach to describe the influence of the ions on the electric response of a cell to an external field is the Poisson-Nernst-Planck (PNP) model. It is based on the equations of continuity for the positive and negative ions and on the equation of Poisson for the actual electric potential across the cell.^{1,2} The PNP model has been proposed to theoretically investigate the dielectric properties of solids and liquids characterized by ionic conduction. The experiments to measure the dielectric properties are performed using the impedance spectroscopy technique, where the external voltage is a simple harmonic function of small amplitude. In its original version, PNP model was built assuming that the electrodes are completely blocking. The model has been recently inferred incorporating a finite speed of response propagation (hyperbolic diffusion regime).³ The case where the diffusion of the ions is governed by fractional diffusion equations has been considered too.⁴ An extension of the model to take into account the non-blocking character of the electrodes was proposed by several authors,⁵⁻⁹ assuming that, in the low frequency region, the conduction current density of ionic origin, at the time t , depends on the surface properties at the same time t . In this

framework, two phenomenological models have been proposed to describe the real nature of the electrodes in which a conduction current exists. In the first model, developed by Chang and Jaffe,⁵ the conduction current is proportional to the variation of the bulk concentration of ions just in front of the electrode. This model reminds Newton's law for the external thermal conduction, or the model used to investigate the evaporation in liquids.¹⁰ In the second model, called Ohmic model, the conduction current is assumed proportional to the surface electric field. According to this model, the electrolytic solution-electrode interface is characterized by an electric conductivity responsible for the dc current across the cell.⁹ The equivalence between these two models has been discussed in Refs. 11–13. However, the conduction current across the electrodes is limited by energy barriers which determine the activation energy of the corresponding electrochemical reactions responsible for the processes of charge transfer between the solution and the external circuit.^{14,15} An accumulation of the charge carriers in the electrode-electrolyte interface develops the electrode polarization which, in turn, influences the transport properties of the ions in bulk materials.^{16,17} It outcomes that the conduction current across the electrode, in the linear approximation, contains two contributions: one proportional to the variation of the bulk concentration of ions in front to the electrode, as in the Chang-Jaffe model, and another proportional to the surface electric field, as in the Ohmic model.¹³ The electric impedance of a cell when the conduction current is regulated by these mixed boundary conditions has not been reported until now. Our aim is to evaluate the impedance of a cell when the non-blocking character of the electrodes is described by these new boundary conditions, and to investigate the relation between our model

and the previously reported expression for the impedance in the Chang-Jaffe and Ohmic cases.

As discussed above, our analysis is based on the assumption that the conduction current across the electrodes, at the time t , depends on the properties of the electrodes at the same time t , i.e., memory effects are not taken into account. This is, of course, an oversimplification of the problem. Recently, several papers concerning the use of the PNP model to interpret the impedance spectroscopy data in which the bulk diffusion of mobile ions is governed by fractional diffusion equation of distributed order and the boundary conditions at the electrodes are described by integro differential equations governing the kinetics at the electrodes have been published.^{18–21} This general approach allows, in principle, to describe adsorption-desorption processes, memory effects, and non-Debye relaxation, by a suitable modification of the kernel appearing in the boundary conditions. The theoretical approach presented in Refs. 18–21 is more fundamental than the one based on the assumption that no hysteretic effects exists in the kinetic governing the charge exchange between the electrolytic solution and the external circuit across the electrode. However, we are convinced that, for practical application, a model for the conduction current limited by energy barriers which determine the activation energy of the corresponding electrochemical reactions, involving only two phenomenological parameters, can be useful to analyze experimental data. The reason is that, at the present, there are no physical models giving useful suggestions on the choice of the kernel to use, and on the surface current density functional dependence on the bulk concentration of ions or on its time or spatial dependence. In this situation, the model proposed in Ref. 22 cannot be easily used to interpret real experiments, and the agreement claimed between the model and the experimental data not very meaningful.

II. MODEL

To deduce the expression of the electric impedance of an electrolytic cell, we assume that the cell is in the shape of a slab, only the positive ions are mobile, and there is not selective adsorption from the electrodes, in such a manner that, in the absence of external electric field the sample is locally neutral. As discussed in Ref. 23, the one-mobile ion approximation is equivalent to the two mobile ion case, when the limiting electrodes have identical properties with respect to the positive and negative ions. We use a Cartesian reference frame having the origin in the middle of the sample, with the z -axis normal to the limiting electrodes situated at $z = \pm d/2$, of surface area S . We indicate by N the bulk concentration of ions in thermodynamic equilibrium, by n the actual bulk concentration of ions in the presence of the external electric field, and by V the electric potential. The

physical parameters of the medium are the electric charge of the ions, q , the dielectric constant of the liquid in which the ions are dispersed, ϵ , and the diffusion coefficient D of the ions in the electrolytic solution. We assume that, in the frequency range considered in our analysis, the medium is not dispersive, i.e., ϵ is frequency independent. In this framework, the bulk partial differential equations of the PNP model are, in the linearized version²

$$\frac{\partial n}{\partial t} = D \left(\frac{\partial^2 n}{\partial z^2} - \frac{qN}{K_B T} \frac{\partial^2 V}{\partial z^2} \right), \quad (1)$$

which is the continuity equation for the positive ions, with $K_B T$ is the thermal energy, and

$$\frac{\partial^2 V}{\partial z^2} = -\frac{q}{\epsilon} (n - N), \quad (2)$$

which is Poisson's equation. We assume that the sample is subjected to an external power supply $\Delta V(t) = \pm (V_0/2) \exp(i\omega t)$, where V_0 is the amplitude of the external voltage, assumed so small that $|n - N| \ll N$ and, hence, the problem can be linearized, and $\omega = 2\pi f$ is the circular frequency of the external voltage of frequency f . The ionic current density is

$$j = -D \left(\frac{\partial n}{\partial z} - \frac{qN}{K_B T} \frac{\partial V}{\partial z} \right). \quad (3)$$

The boundary conditions of the problem are

$$V(\pm d/2, t) = \pm (V_0/2) \exp(i\omega t), \quad (4)$$

on the potential, and

$$j(\pm d/2, t) = \pm \kappa [n(\pm d/2, t) - N] + sE(\pm d/2, t), \quad (5)$$

on the surface concentration of ionic current, where κ and s are the phenomenological parameters entering, respectively, the Chang-Jaffe and Ohmic models, and $E(\pm d/2, t) = -(\partial V / \partial z)_{\pm d/2}$ is the surface electric field.¹³ Note that Chang-Jaffe and Ohmic approaches are, from the mathematical point of view, different. In fact, the boundary condition of the Chang-Jaffe model involves the surface value of the bulk concentration of ions, whereas that of the Ohmic model involves the spatial derivative of the electric potential.

The impedance of the cell can be evaluated operating in the usual manner, by solving Eqs. (1) and (2) with the boundary conditions (4) and (5), as discussed in Ref. 24. To write the expression of the electric impedance of the cell in terms of dimensionless parameters, we define $\Lambda = \sqrt{\epsilon K_B T / (Nq^2)}$, which is the Debye length for the present case, and $\omega_D = D / \Lambda^2$ is the Debye circular frequency. We introduce, furthermore, $M = d / (2\Lambda)$, $\omega_c = qs / \epsilon$, and $\omega_\kappa = \kappa / \Lambda$. Setting $\Omega = \omega / \omega_D$, $\Omega_c = \omega_c / \omega_D$ and $\Omega_\kappa = \omega_\kappa / \omega_D$, the electric impedance of the cell is given by

$$Z = \mathcal{R}_\infty \frac{M(\Omega_c + i\Omega)\sqrt{1+i\Omega} + (1 - \Omega_c + M\Omega_\kappa\sqrt{1+i\Omega}) \tanh(M\sqrt{1+i\Omega})}{M\sqrt{1+i\Omega}(\Omega_c + i\Omega + \Omega_\kappa\sqrt{1+i\Omega} \tanh(M\sqrt{1+i\Omega}))}, \quad (6)$$

where $\mathcal{R}_\infty = (1/\epsilon\omega_D)(d/S)$.

III. MODELS OF CHANG-JAFFE AND OHMIC AS PARTICULAR CASES

From Eq. (6), putting $\Omega_c = 0$, i.e., assuming that the boundary conditions (5) are of the Chang-Jaffe type, we get

$$Z_{CJ} = \mathcal{R}_\infty \frac{iM\Omega\sqrt{1+i\Omega} + [1 + M\Omega_\kappa(1+i\Omega)] \tanh(M\sqrt{1+i\Omega})}{M(1+i\Omega)^{3/2} [i\Omega + \Omega_\kappa\sqrt{1+i\Omega} \tanh(M\sqrt{1+i\Omega})]}, \quad (7)$$

coinciding with the impedance predicted by the Chang-Jaffe model.¹¹ On the contrary, if $\Omega_\kappa = 0$, i.e., assuming that the boundary conditions (5) are of Ohmic type, from Eq. (6) we obtain

$$Z_O = \mathcal{R}_\infty \frac{M(\Omega_c + i\Omega)\sqrt{1+i\Omega} + (1 - \Omega_c)\tanh(M\sqrt{1+i\Omega})}{M(1+i\Omega)^{3/2}(\Omega_c + i\Omega)}, \quad (8)$$

coinciding with the impedance predicted by the Ohmic model.¹¹ From this discussion, it follows that expression (6) for the electric impedance of the cell contains, as particular cases, the Chang-Jaffe and Ohmic models. Using Eqs. (7) and (8), and imposing that $Z_{CJ} = Z_O$, it is possible to find the correspondence between Ω_κ and Ω_c , i.e., between κ and s , appearing in the Chang-Jaffe and Ohmic models. A simple calculation shows that the equivalence between the two models exists for

$$\Omega_\kappa^* = \frac{\Omega_c \sqrt{1+i\Omega} \coth(M\sqrt{1+i\Omega})}{1 - \Omega_c}. \quad (9)$$

As pointed out in Ref. 11, to a real and frequency independent Ω_c corresponds a complex and frequency dependent Ω_κ^* . However, since the non-blocking properties of the electrodes are important only in the dc limit ($\Omega \rightarrow 0$), from Eq. (9) we get that in this limit $\Omega_\kappa^* = \Omega_c$, since in real situations $M \gg 1$. In this case, the spectra of the real, R , and imaginary, X , parts of the electric impedance of the cell coincide on all the frequency range.

IV. CORRESPONDENCE BETWEEN THE PRESENT MODEL AND OHMIC MODEL

To find the correspondence between the mixed boundary conditions model and the pure Ohmic model, it is necessary to equate Z given by Eq. (6) to Z_O given by Eq. (8) and solve it for the phenomenological parameter of the Ohmic model appearing in Eq. (8). A simple calculation gives for the equivalent pure Ohmic model phenomenological parameter the expression

$$\Omega_c^* = \frac{\Omega_c \sqrt{1+i\Omega} + \Omega_\kappa \tanh(M\sqrt{1+i\Omega})}{\sqrt{1+i\Omega} + \Omega_\kappa \tanh(M\sqrt{1+i\Omega})}. \quad (10)$$

In Fig. 1, the frequency dependencies of the real, $S_r = \Re[\Omega_c^*]$, and imaginary, $S_i = \Im[\Omega_c^*]$, parts of Ω_c^* are reported for $\Omega_c = 10^{-2}$ and $\Omega_\kappa = 3 \times \Omega_c$. As it follows from the quoted figure, $S_r = S_r(\Omega)$ is a monotonic decreasing function of Ω , whereas the modulus of $S_i = S_i(\Omega)$ tends to zero in the dc limit as well as in the high frequency region, and presents a maximum

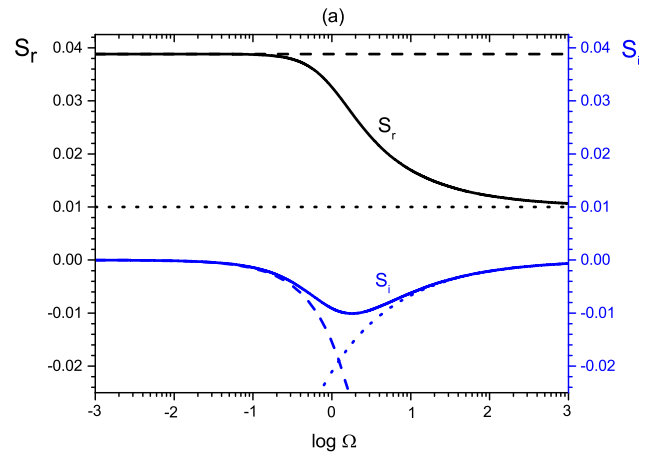


FIG. 1. Frequency dependence of real (black) and imaginary (blue) parts of Ω_c^* . Dashed: $\Omega \rightarrow 0$, dotted: $\Omega \rightarrow \infty$.

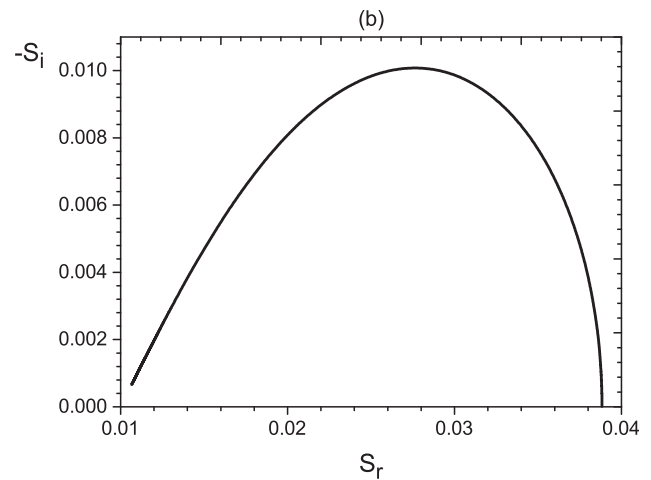


FIG. 2. Parametric plot $S_i = S_i(S_r)$.

close to the frequency of Debye. They are such that, in the limit of large M ,

$$\lim_{\Omega \rightarrow 0} S_r = \frac{\Omega_c + \Omega_\kappa}{1 + \Omega_\kappa}, \quad \lim_{\Omega \rightarrow \infty} S_r = \Omega_c, \quad \text{and} \\ \lim_{\Omega \rightarrow 0} S_i = -\frac{\Omega_\kappa(1 - \Omega_c)}{2(1 - \Omega_\kappa)^2} \Omega, \quad \lim_{\Omega \rightarrow \infty} S_i = -\frac{\Omega_\kappa(1 - \Omega_c)}{\sqrt{2}\Omega}. \quad (11)$$

The parametric plot $S_i = S_i(S_r)$ is shown in Fig. 2. If we compare the predictions of the complete model with those of the equivalent pure Ohmic model using for $\Omega_c^* = \lim_{\Omega \rightarrow 0} S_r$, the agreement is good on all frequency range. Similar consideration is valid when the general model is compared with a pure Chang-Jaffe model, in the sense that it is possible to find a ω_κ^* such that the predictions of the two models coincide on all frequency range.

V. CONCLUSIONS

We have considered the electric response of an electrolytic cell limited by non-blocking electrodes to an external periodic electric excitation of small amplitude. We have assumed that the conduction current across the electrodes is

limited by energy barriers which determine the activation energy of the corresponding electrochemical reactions responsible for the processes of charge transfer between the solution and the external circuit. From this hypothesis, it follows that the boundary conditions describing the non-blocking character of the electrodes are, in the linear limit, a combination of the boundary conditions used in the Chang-Jaffe and Ohmic model. In this general framework, we obtained the expression for the electrical impedance of the cell. This expression contains, as particular cases, the impedance proposed for the Chang-Jaffe and Ohmic models. We have also shown that the predictions of the general model, with mixed boundary conditions, can be recovered by a pure Ohmic model, with a particular value of the Ohmic phenomenological parameter. Even if the equivalence between the models requires that the Ohmic parameter has to be, in principle, complex and frequency dependent, a good correspondence can be reached also with a real and frequency independent phenomenological parameter for the pure Ohmic model. The conclusion of our investigation is that the processes taking place at the electrodes, responsible for the conduction current across the electrodes, are related both to the surface electric field and to the variation of the bulk concentration of ions just in front of the electrodes. However, without further experimental information it is not possible to separate the two contributions considering only the impedance spectroscopy data.

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