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Significance of small voltage in impedance spectroscopy measurements on electrolytic cells

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We investigate, theoretically, for what amplitude of the applied voltage to an electrolytic cell the concept of impedance is meaningful. The analysis is performed by means of a continuum model, by assuming the electrodes perfectly blocking. We show that, in the low-frequency range, the electrolytic cell behaves as a linear system only if the amplitude of the measurement voltage is small with respect to the thermal voltage $V_T = k_B T / q$, where $k_B T$ is the thermal energy, and q is the modulus of the electrical charge of the ions, assumed identical except for the sign of the charge. On the contrary, for large frequency, we prove that the amplitude of the applied signal has to be small with respect to a critical voltage that is frequency dependent. The same kind of analysis is presented for the case in which the diffusion coefficients of the positive ions is different from that for negative ions, and for the case where surface adsorption takes place. © 2005 American Institute of Physics. [DOI: 10.1063/1.2137444]

I. INTRODUCTION

The impedance spectroscopy technique is used to characterize the electrical properties of materials and their interfaces with the electrodes.¹ According to this technique, an external voltage is applied to the sample, and the electrical current detected. In the limit of small applied voltage, the electrical current is proportional to the applied voltage. In this framework, the electrical impedance defined by the ratio voltage/current is independent of the amplitude of the applied voltage. Our aim in this paper is to study for what amplitude of the applied voltage an electrolytic cell behaves as a linear system, and hence the concept of electrical impedance is meaningful. Our analysis will be performed by means of a continuum model, in the sense of Ref. 2. The paper is organized as follows. In this Introduction we enumerate the fundamental hypotheses performed to obtain an analytical solution for the fundamental equations of the continuum model for the electrolytic cell. In Sec. II the case in which the positive and negative ions have the same mobility is considered. The generalization of the model to the case in which the mobility of the positive ions is different from the one of the negative ions is discussed in Sec. III. The case in which the surfaces adsorb ions is presented in Sec. IV. The results of the paper are discussed in Sec. V, whereas Sec. VI is devoted to the conclusions.

The influence of the diffuse layer of the ionic charge on the impedance spectroscopy of a cell of liquid has been analyzed in Ref. 3. In the theoretical investigation presented in Ref. 3, it is considered a slab of thickness d filled by an isotropic liquid. The z axis of the Cartesian reference frame used in the description is normal to the bounding surfaces at

$z = \pm d/2$, and it is assumed that in thermodynamical equilibrium the liquid contains a density N of ions of positive and negative sign, uniformly distributed. The ions are assumed to be identical in all the aspects, except for the sign of the electrical charge. In particular, they have the same mobility $\mu_p = \mu_m = \mu$, where p and m indicate positive and negative ions. The surfaces limiting the sample are also assumed identical, with the same adsorption energy with respect to the two types of ions, in order to avoid the problems connected with the selective ion adsorption.^{4,5} In this situation the liquid is globally and locally neutral. The presence of an external electric voltage produces a perturbation of the distribution of the ions in the liquid, in the sense that it remains globally neutral, but now it is locally charged.⁶ In the following we suppose that the sample is submitted to an external sinusoidal voltage of amplitude V_0 and frequency $f = \omega/(2\pi)$. By indicating with n_p and n_m the densities of the two kinds of ions, we have $n_p(z, t) = n_m(z, t) = N$, for $V_0 = 0$, and $n_p(z, t) \neq n_m(z, t)$, for $V_0 \neq 0$.

II. CASE IN WHICH THE IONS HAVE THE SAME DIFFUSION COEFFICIENT: $D_p = D_m = D$

The fundamental equations of the problem are the equation of continuity,

$$\frac{\partial n_r}{\partial t} = - \frac{\partial j_r}{\partial z}, \quad (1)$$

where $r = p, m$, and the equation of Poisson,

$$\frac{\partial^2 V}{\partial z^2} = -\frac{q}{\varepsilon}(n_p - n_m), \quad (2)$$

where q is the electrical charge of the ions, and j_r the density of currents of positive ($r=p$) and negative ($r=m$) ions given by

$$j_r = -D \left(\frac{\partial n_r}{\partial z} \pm \frac{q}{k_B T} n_r \frac{\partial V}{\partial z} \right), \quad (3)$$

with $+$ for $r=p$ and $-$ for $r=m$.³ Since the electrodes are supposed perfectly blocking, we have the following boundary conditions on j_r :

$$j_r(\pm d/2, t) = 0. \quad (4)$$

The other boundary conditions of the problem are connected with the imposed difference of potential that we assume of the type

$$V(\pm d/2, t) = \pm (V_0/2) \exp(i\omega t). \quad (5)$$

As discussed in Ref. 3, the equation of continuity is nonlinear. Hence, for arbitrary applied voltage the cell does not behave as a linear system. Only in the case in which in the presence of the external voltage the actual ionic densities, $n_r = N + \delta n_r(z, t)$, are such that $\delta n_r(z, t) \ll N$, the system behaves in a linear manner, and the concept of electrical impedance is meaningful. In this framework Eq. (1) and Eq. (2), by taking into account Eq. (3), can be rewritten as

$$\begin{aligned} \frac{\partial \delta n_r(z, t)}{\partial t} &= -D \left(\frac{\partial^2 \delta n_r(z, t)}{\partial z^2} \pm \frac{qN}{k_B T} \frac{\partial^2 V(z, t)}{\partial z^2} \right), \\ \frac{\partial^2 V(z, t)}{\partial z^2} &= -\frac{q}{\varepsilon} [\delta n_p(z, t) - \delta n_m(z, t)], \end{aligned} \quad (6)$$

which are now linear. We look for solutions of Eqs. (6) of the type $\delta n_r(z, t) = \eta_r(z) \exp(i\omega t)$ and $V(z, t) = \phi(z) \exp(i\omega t)$. By substituting these trial functions in Eqs. (6), we get

$$\begin{aligned} i\omega \eta_r(z) &= -D \left(\eta_r''(z) \pm \frac{qN}{k_B T} \phi''(z) \right), \\ \phi''(z) &= -\frac{q}{\varepsilon} [\eta_p(z) - \eta_m(z)]. \end{aligned} \quad (7)$$

Equations (6) form a system of ordinary differential equations with constant coefficients. In the case under consideration, where $D_p = D_m$, the condition $V(d/2, t) = -V(-d/2, t)$ implies $V(z, t) = -V(-z, t)$ and $n_p(z, t) = n_m(-z, t)$. It follows that $\eta_+(z) = \eta_-(-z)$. A standard analysis gives

$$\begin{aligned} \eta_r(z) &= \pm p_0 \sinh(\beta z), \\ \phi(z) &= -2(q/\varepsilon \beta^2) p_0 \sinh(\beta z) + cz, \end{aligned} \quad (8)$$

where $\beta = (1/\lambda) \sqrt{1 + i(\omega/D)\lambda^2}$, and $\lambda = \sqrt{\varepsilon k_B T / (2Nq^2)}$ is the length of Debye. The coefficients p_0 and c appearing in Eqs. (8), are determined by means of the boundary conditions (4) and (5) and are found to be

$$p_0 = -\frac{Nq\beta}{2k_B T (1/\lambda^2 \beta) \sinh(\beta d/2) + i(\omega d/2D) \cosh(\beta d/2)} V_0,$$

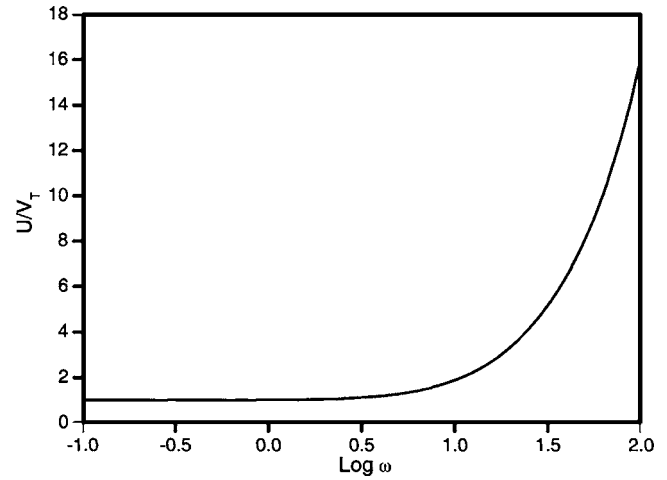


FIG. 1. Frequency dependence of the critical voltage U for an electrolytic cell. In the low frequency region $U(\omega \rightarrow 0) = V_T [1 + (1/2)(\lambda d \omega / 2D)^2]$. On the contrary, in the high-frequency range, $U(\omega \rightarrow \infty) = V_T \sqrt{\omega d^2 / D}$. The curve is drawn for $q = 1.6 \times 10^{-19}$ A s (monovalent ions), $N = 4.2 \times 10^{20} \text{ m}^{-3}$, $\varepsilon = 6.7 \times \varepsilon_0$, $T = 300$ K, $d = 25 \text{ } \mu\text{m}$, $S = 2 \times 10^{-4} \text{ m}^2$, and $D_p = D_m = 8.2 \times 10^{-12} \text{ m}^2/\text{s}$. The logarithms are in base 10 and ω is in rad/s.

$$c = i \frac{\omega}{2D (1/\lambda^2 \beta) \sinh(\beta d/2) + i(\omega d/2D) \cosh(\beta d/2)} V_0, \quad (9)$$

as reported in Ref. 8

We can now investigate for what amplitude of the applied signal the condition $\delta n_r(z, t) \ll N$ is verified. Since $\delta n_r(z, t) = \eta_r(z) \exp(i\omega t)$, the maximum variation of $\delta n_r(z, t)$ is $|\delta n_r(z, t)| = 2|\eta_r(z)| \leq |p_0 \sinh(\beta d/2)|$. Consequently, the condition we are looking for is, by taking into account (9),

$$V_0 \leq U = V_T \left| \frac{1}{\lambda^2 \beta^2} + i \frac{\omega d}{2D \beta} \coth\left(\beta \frac{d}{2}\right) \right|, \quad (10)$$

where $V_T = k_B T / q$ is the thermal voltage. For a numerical analysis of the analysis presented above, we suppose that $q = 1.6 \times 10^{-19}$ A s (monovalent ions), $N = 4.2 \times 10^{20} \text{ m}^{-3}$, $\varepsilon = 6.7 \times \varepsilon_0$, $T = 300$ K, $d = 25 \text{ } \mu\text{m}$, and $S = 2 \times 10^{-4} \text{ m}^2$.⁹ With these values for the physical parameters, relevant to a commercial 5CB nematic liquid crystal, the length of Debye is $\lambda \sim 1.05 \times 10^{-7} \text{ m}$. In Fig. 1 we show the frequency dependence of U by assuming $D_p = D_m = 8.2 \times 10^{-12} \text{ m}^2/\text{s}$.⁹ As it is evident from this figure, in the limit of $\omega \rightarrow 0$, U tends to V_T , as expected. In fact, in this region the profile of the electric potential is given by the Poisson–Boltzmann equation, where the thermal energy $k_B T$ is compared with the electrostatic energy qV . On the contrary, for large ω , U diverges as $\omega^{1/2}$. By means of (10) we get, in the limit of $d \gg \lambda$, the asymptotic expressions

$$\begin{aligned} U(\omega \rightarrow 0) &= V_T \left[1 + \frac{1}{2} \left(\frac{\lambda d}{2D} \right)^2 \omega^2 \right], \\ U(\omega \rightarrow \infty) &= \frac{1}{2} V_T \frac{d}{\sqrt{D}} \sqrt{\omega}. \end{aligned} \quad (11)$$

From the previous discussion, it follows that if the investigations on the dielectric properties of the material have to be performed in the very low-frequency region, the amplitude of the signal applied to the sample has to be small with

respect to $k_B T/q$. On the contrary, for large ω this condition is substituted by a new one, which depends on the frequency.

III. CASE IN WHICH THE IONS HAVE DIFFERENT DIFFUSION COEFFICIENT: $D_p \neq D_m$

The analysis presented previously can be generalized to the situation in which the mobilities of the positive ions, D_p , is different from that of the negative ions, D_m . In this case, j_r are given by

$$j_r = -D_r \left(\frac{\partial n_r}{\partial z} \pm \frac{q}{k_B T} n_r \frac{\partial V}{\partial z} \right). \quad (12)$$

The fundamental equations of the problem are still Eq. (1) and Eq. (2), which have to be solved with the boundary conditions (4) and (5). By assuming again that $\delta n_r(z, t) \ll N$, the profiles of the bulk densities of ions and of the electric potential are given by

$$\eta_p(z) = C_1 \sinh(\gamma_1 z) + C_2 \sinh(\gamma_2 z),$$

$$\eta_m(z) = k_1 C_1 \sinh(\gamma_1 z) + k_2 C_2 \sinh(\gamma_2 z), \quad (13)$$

$$\phi(z) = -\frac{q}{\varepsilon} \left(\frac{1-k_1}{\gamma_1^2} C_1 \sinh(\gamma_1 z) + \frac{1-k_2}{\gamma_2^2} C_2 \sinh(\gamma_2 z) \right) + Az, \quad (14)$$

respectively, as it has been shown in Ref. 10. The integration constants C_1 , C_2 , and A are given by the boundary conditions (4) and (5). In (13) and (14) the parameters γ_1 , γ_2 , k_1 , and k_2 are

$$\gamma_{1,2} = \sqrt{\frac{1}{2} \left(\frac{1}{\ell_p^2} + \frac{1}{\ell_m^2} \right)} \pm \sqrt{\left[\frac{1}{2} \left(\frac{1}{\ell_p^2} - \frac{1}{\ell_m^2} \right) \right]^2 + \frac{1}{4\lambda^4}} \quad (15)$$

and

$$k_{1,2} = -2\lambda^2 \left(\gamma_{1,2}^2 - \frac{1}{\ell_p^2} \right), \quad (16)$$

where $\ell_\alpha^2 = 2\lambda^2 / [1 + 2i(\omega/D_\alpha)\lambda^2]$. By imposing again the condition $2|\eta_r(z)| \ll N$, we obtain the critical voltage U such that the system under investigation can be considered linear when $V_0 \ll U$. The results of the numerical calculations are reported in Fig. 2, by assuming for the physical parameters of the sample again the ones reported above, and $D_p = 10D_m = 8.2 \times 10^{-11} \text{ m}^2/\text{s}$.¹¹ Again, in the low-frequency range $U \rightarrow V_T$, whereas for large ω , U increases as $\sqrt{\omega}$, according to (11), with D_p or D_m . Hence, the critical voltage depends on the larger diffusion coefficient.

IV. CASE IN WHICH THE SURFACES ADSORB IONS

Finally, we can consider the case in which at the electrodes there is adsorption of particles. In this case, by indicating with $\sigma_r(\pm d/2, t)$, the surface density of adsorbed particles, instead of the boundary conditions (4) we have now,

$$j_r(\pm d/2, t) = \frac{d\sigma_r(\pm d/2, t)}{dt}. \quad (17)$$

In the Langmuir's approximation,

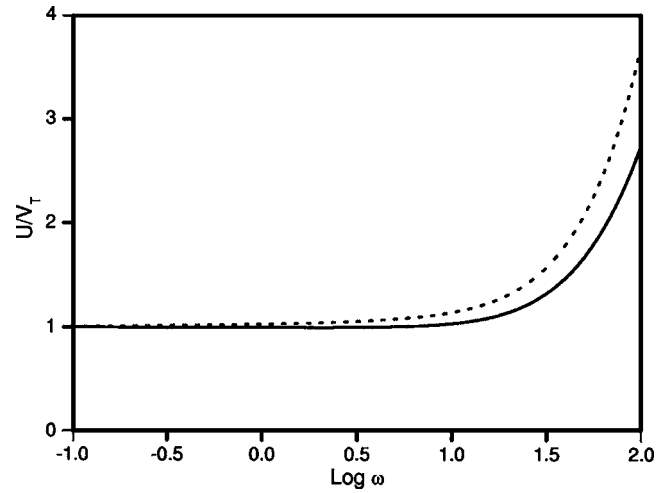


FIG. 2. The same as in Fig. 1, when $q = 1.6 \times 10^{-19} \text{ A s}$ (monovalent ions), $N = 4.2 \times 10^{20} \text{ m}^{-3}$, $\varepsilon = 6.7 \times \varepsilon_0$, $T = 300 \text{ K}$, $d = 25 \text{ }\mu\text{m}$, $S = 2 \times 10^{-4} \text{ m}^2$, and $D_p = 10D_m$. The dotted line corresponds to the case $D_p = D_m = 8.2 \times 10^{-12} \text{ m}^2/\text{s}$. The continuous line corresponds to the case $D_p = 10D_m = 8.2 \times 10^{-11} \text{ m}^2/\text{s}$. The logarithms are in base 10 and ω is in rad/s.

$$\frac{d\sigma_r(\pm d/2, t)}{dt} = k n_r(\pm d/2, t) - \frac{1}{\tau} \sigma_r(\pm d/2, t), \quad (18)$$

where k and τ are the adsorption coefficient and the desorption time, respectively.¹³ In this framework, the profiles of the ionic densities and of the electrical potential across the sample are still given by (8), where p_0 and c follow from the boundary conditions (5), (17), and (18), and are

$$\left[1 + \beta \frac{k\tau}{1 + i\omega\tau} \tanh\left(\frac{\beta d}{2}\right) \right] p_0 - i \frac{Nq/(k_B T)}{(\omega/D\beta) \cosh(\beta d/2)} c = 0,$$

$$-2 \frac{q}{\varepsilon \beta^2} \sinh\left(\frac{\beta d}{2}\right) p_0 + \frac{d}{2} c = V_0/2, \quad (19)$$

where N is now the bulk density of ions in the absence of an external electrical voltage, as discussed in Ref 12. By imposing, as in the previous cases, the condition $2|\eta_r(z)| \ll N$, we obtain the critical voltage U such that the system under investigation can be considered linear when $V_0 \ll U$. The result of the numerical calculations is reported in Fig. 3, by assuming for the physical parameters of the sample again the ones reported above, with $D_p = D_m = 8.2 \times 10^{-12} \text{ m}^2/\text{s}$,⁹ $k = 10^{-6} \text{ m s}^{-1}$ and $\tau = 0.1$.¹³ As expected in the low-frequency range $U \rightarrow V_T$. In the high-frequency range, U is still given by (11). The maximum deviation of the present U with respect to the one relevant to the case in which the adsorption is absent takes place for a frequency $\omega \sim 1/\tau$.

V. DISCUSSION

The important point in the analysis presented previously is that in the problem under investigation there is an intrinsic voltage U . For $V_0 \ll U$ the system behaves in a linear manner, and the concept of electrical impedance is useful. When the condition $V_0 \ll U$ is not satisfied, the system behave in a non-linear way. This means that if $V(\pm d/2, t) = \pm (V_0/2) \exp(i\omega t)$,

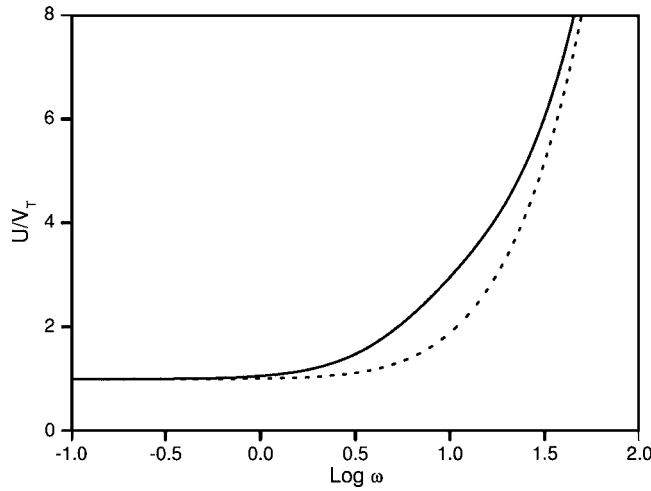


FIG. 3. The same as in Fig. 1, when the adsorption phenomenon is taken into account, in the Langmuir's approximation, by assuming $q=1.6 \times 10^{-19}$ A s (monovalent ions), $N=4.2 \times 10^{20} \text{ m}^{-3}$, $\epsilon=6.7 \times \epsilon_0$, $T=300$ K, $d=25 \text{ } \mu\text{m}$, $S=2 \times 10^{-4} \text{ m}^2$, and $D_p=D_m=8.2 \times 10^{-12} \text{ m}^2/\text{s}$. In the low- and high-frequency ranges the critical voltage U is still given by (11). The maximum influence of the adsorption effect on U is localized around the frequency $\omega \sim 1/\tau$. The continuous curve corresponds to the case where $k=10^{-6} \text{ m s}^{-1}$ and $\tau=0.1 \text{ s}$, whereas the dotted line corresponds to the case in which the adsorption phenomenon is absent. The logarithms are in base 10 and ω is in rad/s.

$\delta n_r(z, t)$, and $V(z, t)$ are not harmonic functions with frequency $f=\omega/(2\pi)$. In this case $\delta n_r(z, t)$ and $V(z, t)$ are of the type

$$\delta n_r(z, t) = \sum_h \eta_{r,h}(z) \exp(ih\omega t),$$

$$V(z, t) = \sum_h \phi_h(z) \exp(ih\omega t), \quad (20)$$

where $\eta_{r,1}(z)=\eta(z)$ and $\phi_1(z)=\phi(z)$, introduced previously.

It was possible to analyze the problem in a more technical way, according to the following scheme. By substituting expansions (20) into (1) and (2) and into the boundary conditions (4) and (5) one obtains a cascade of differential equations and the relevant boundary conditions for $\eta_{r,h}(z)$ and $\phi_h(z)$. For $h=1$ the equations are

$$i\omega \eta_{r,1}(z) = D \left(\eta_{r,1}''(z) \pm \frac{qN}{k_B T} \phi_1''(z) \right),$$

$$\phi_1''(z) = -\frac{q}{\epsilon} [\eta_{p,1}(z) - \eta_{m,1}(z)], \quad (21)$$

where, as before, for $r=p$ there is the sign +, and for $r=m$ the sign -. Equations (21) have to be solved with the boundary conditions at $z=\pm d/2$,

$$\phi_1 = \pm V_0/2, \quad \eta_{r,1}' \pm (qN/k_B T) \phi_1 = 0, \quad (22)$$

as we have done in Sec. II. For $h=2$ one gets

$$2i\omega \eta_{r,2}(z) = D \left(\eta_{r,2}''(z) \pm \frac{qN}{k_B T} \phi_2''(z) \right) \\ \pm \frac{Dq}{k_B T} [\eta_{r,1}(z) \phi_1'(z)],$$

$$\phi_2''(z) = \frac{q}{\epsilon} [\eta_{p,2}(z) - \eta_{m,2}(z)], \quad (23)$$

with the boundary conditions at $z=\pm d/2$

$$\phi_2 = 0, \quad \eta_{r,2} \pm (qN/k_B T) [\phi_2' + (\eta_{r,1}/N) \phi_1'] = 0. \quad (24)$$

In the same manner it is possible to obtain the bulk differential equations and the boundary conditions for all h . By means of $\eta_{r,h}(z)$ and $\phi_h(z)$ it is possible to evaluate the electrical current in the external circuit $I(t)$, and hence to determine the electrical impedance of the cell defined by $Z = V_0 \exp(i\omega t)/I(t)$. Since $I(t)$ is not a harmonic function of t with frequency $f=\omega/(2\pi)$, it follows that $Z=Z(t)$. At this point, knowing the accuracy of the used experimental setup, it is possible to determine the maximum amplitude, V_M , for which the system under investigation does not behave in a nonlinear manner. It is clear that this procedure is, in some way, arbitrary, since it depends on the experimental setup. On the contrary, our analysis, based on the condition $\delta n_r \ll N$, proves the existence of an intrinsic voltage with which it is necessary to compare the amplitude of the applied voltage.

In the discussion presented previously, we have considered, for simplicity, the case in which the diffusion coefficients of the positive and negative ions are the same, and the adsorption phenomenon is absent. However, a simple inspection shows that it is valid also in the case where $D_p \neq D_m$ and when the adsorption phenomenon is present.

VI. CONCLUSION

By means of a continuum model we have analyzed what means "small voltage" in the impedance spectroscopy measurements on an electrolytic cell. Actually our analysis is of some interest for all systems in which the ionic contribution to the total current is not negligible, as the liquid crystals.

We have shown that, in the low-frequency range, the applied voltage has to be small with respect to the thermal voltage $V_T=k_B T/q$. In the high-frequency region, the applied voltage has to be small with respect to the critical voltage diverging as the square root of the frequency. Our analysis has been performed by considering the case in which the $D_p=D_m=D$, as well as the case in which $D_p \neq D_m$. We have also considered the case in which the limiting surface of the liquid can absorb ions. The analysis presented in our paper is simple, however, it was not previously presented. The results are rather important from an experimental point of view. In fact, as it has been stressed previously in this paper, the impedance spectroscopy technique is meaningful only if it is possible to define the electrical impedance of the cell under investigation. This implies that the system behaves as a linear system. If this condition is not satisfied, the analysis of the experimental data is more complex, and it has to be done, taking into account the nonlinear character of the system under investigation. In recent papers devoted to the impedance spectroscopy analysis of different systems the applied voltage to the cell cannot be considered small in the frequency range where the measurements are performed.^{11,14-16}

Consequently, the systems cannot be considered as linear systems, and some of the conclusions derived in Refs. 11 and 14–16 could be not correct.

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