# Comment on "Modeling of electrode polarization for electrolytic cells with a limited ionic adsorption"

A. L. Alexe-Ionescu,[1,2] G. Barbero,[2,3] and I. Lelidis[2,3]

[1]*University Politehnica of Bucharest, Faculty of Applied Sciences, Splaiul Independentei 313, 060042 Bucharest, Romania*
[2]*Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy*
[3]*Department of Physics, Solid State Section, University of Athens, Panepistimiopolis, Zografos, Athens 157 84, Greece*

Recently, Sawada [Phys. Rev. E **88**, 032406 (2013)] proposed a model to take into account the dielectric dispersion of ionic origin in a weak electrolyte cell. We first show that the model is based on questionable assumptions. Next, we point out an error in the author's calculation of the current in the external circuit. Finally, we demonstrate why some criticism on recent papers is irrelevant.

In recent papers, Sawada reports on the electric response of a cell of chlorobenzene doped with different concentrations of tetrabutylammonium tetraphenylborate (TBATPB) [1–3]. According to the presented experimental data, the real and imaginary parts of the complex dielectric constant present two relaxations. The one in the higher frequency region depends on the ionic concentration, whereas that in the dc limit is independent of it. This observation is of some interest. In Ref. [1], Sawada interprets his experimental data assuming that, by increasing the concentration of TBATPB, there is an increasing number of different type ionic groups contributing to the electrical response of the cell. The analysis was based assuming the validity of the superposition principle. In Ref. [4], we have shown that, in the low frequency region, the superposition principle does not work. Consequently, the interpretation of the data proposed in Ref. [1] does not work well. The same set of experimental data has been considered in Ref. [2] and has been fitted again by means of the model presented in Ref. [1], based on the assumption of a constant electric field across the sample. The limit of this assumption was discussed in Refs. [5,6]. In Ref. [3], the subject of this Comment, Sawada, points out that his experimental data cannot be interpreted by means of the standard Poisson-Nernst-Planck (PNP) model using a reasonable value of the diffusion coefficient for the ions in chlorobenzene, expected to be on the order of $10^{-9}$ m$^2$/s. The limits of the PNP model have been discussed also in Refs. [7–9]. For this reason, Sawada proposes a modified version of the PNP model, based on the assumptions: (i) The actual electric field across the sample coincides with the external field, and (ii) the interface between the electrolyte and the electrode is responsible for a capacitance, rather small with respect to that of the Stern layer as suggested in Ref. [10].

The aim of our Comment is as follows: (i) to show that the model proposed by Sawada [3] has to be used with caution since the reported expression for the admittance of the cell, used in the analysis of the data, is not correct and (ii) to refute his criticism on Ref. [11].

In Ref. [3], the sample is in the shape of a slab of thickness $d$ and surface area $S$, and the dopant TBATPB is assumed completely dissociated in the solvent. The Cartesian reference frame used in the description has the $x$ axis perpendicular to the electrodes, placed at $x = 0$ and $x = d$. The diffusion coefficients of the positive and negative ions are supposed to be identical $D_p = D_m = D$. In this framework, the presence

of the external voltage of amplitude $V_1$ and circular frequency $\omega$ is responsible for a redistribution of ions. The actual bulk density of positive and negative ions can be written as $n_p(x,t) = c_0 + p(x,t)$ and $n_m(x,t) = c_0 + m(x,t)$, where $c_0$ is the concentration of TBATPB and $p(x,t)$ and $m(x,t)$ are the bulk variations in the ionic densities due to the presence of the external field. In this framework, the fundamental equations of the PNP model take the form

$$\frac{\partial p}{\partial t} = D \frac{\partial}{\partial x}\left\{\frac{\partial p}{\partial x} - \frac{q(c_0 + p)}{K_B T}E\right\}, \qquad (1)$$

$$\frac{\partial m}{\partial t} = D \frac{\partial}{\partial x}\left\{\frac{\partial m}{\partial x} + \frac{q(c_0 + m)}{K_B T}E\right\}, \qquad (2)$$

$$\frac{\partial E}{\partial x} = \frac{q}{\varepsilon}(p - m), \qquad (3)$$

where we have taken into account that $\mu/D = q/(K_B T)$, $K_B$ is the Boltzmann constant, and $T$ is the absolute temperature [12]. In the limit of small $V_1$, the perturbation of the bulk ionic densities due to the external electric field are small: $p \ll c_0$ and $m \ll c_0$. Therefore, $p$ and $m$ can be considered on the same order as $V_1$, as the electric field $E$, and Eqs. (1) and (2), at the first order in the variations, can be rewritten as

$$\frac{\partial p}{\partial t} = D \frac{\partial}{\partial x}\left(\frac{\partial p}{\partial x} - \frac{q c_0}{K_B T}E\right), \qquad (4)$$

$$\frac{\partial m}{\partial t} = D \frac{\partial}{\partial x}\left(\frac{\partial p}{\partial x} + \frac{q c_0}{K_B T}E\right). \qquad (5)$$

In the limit of small $V_1$, the fundamental equations of the model are Eqs. (3)–(5), that are linear with constant coefficients. For a harmonic applied voltage $\Delta V(t) = V_1 \exp(i\omega t)$, the solutions we are looking for are, as assumed in Ref. [3], $p(x,t) = p_1 \exp(i\omega t)$, $m(x,t) = m_1 \exp(i\omega t)$, and $E(x,t) = E_1(x) \exp(i\omega t)$, and the equations to be solved for $p_1(x)$, $m_1(x)$, and $E_1(x)$ are

$$i\frac{\omega}{D}p_1 = p_1'' - \frac{q c_0}{K_B T}E', \qquad (6)$$

$$i\frac{\omega}{D}m_1 = p_1'' + \frac{q c_0}{K_B T}E', \qquad (7)$$

$$E_1' = \frac{q}{\varepsilon}(p_1 - m_1), \qquad (8)$$

where the prime means a derivative with respect to $x$, $f' = df/dx$. Equations (6)–(8) have to be solved with the proper boundary conditions. If the electrodes are perfectly blocking, the current densities have to vanish on the electrodes. In this case, in the linear approximation of the PNP, the boundary conditions at $x = 0$ and $x = d$ are

$$p_1' - \frac{qc_0}{K_BT}E_1 = 0, \quad m_1' + \frac{qc_0}{K_BT}E_1 = 0, \qquad (9)$$

with $V(0) = 0$ and $V(d) = V_1$ for the electric potential, related to the electric field by $E_1 = -V'$. On the contrary, if the electrodes are adsorbing, the boundary conditions at $x = 0$ and $x = d$ are

$$p_1' - \frac{qc_0}{K_BT}E_1 = \pm\beta^* p_1, \quad m_1' + \frac{qc_0}{K_BT}E_1 = \pm\beta^* m_1, \quad (10)$$

where $\beta^* = \xi^*/D$ is the parameter related to the adsorption [3,13]. The equations of the problem form a system of linear differential equations with linear boundary conditions. The problem can be analytically solved [11,14,15], contrary to the statement in Ref. [3].

In Ref. [3], it is assumed that the actual electric field across the sample is position independent and is given by $E_1 = V_1/d$. Consequently, the actual electric field is independent of the ions' distribution. According to Ref. [3], this is a reasonable approximation. Our opinion about this approximation is different. In the limit of a small external electric field, the ions move under the effect of the electric force until the actual electric field vanishes in the bulk. In the limit of a large external field, the ions are unable to screen it, and the electric field in the sample is nearly uniform. However, in this limit, the bulk variation in densities of the ions is large, and hence the linear approximation does not work any longer [16]. We stress that, in Ref. [3], the system is not assumed supported [17] because, in the bulk, the field is not screened by the ions. In this framework, Eqs. (6)–(8) are

$$i\frac{\omega}{D}p_1 = p_1'', \quad i\frac{\omega}{D}m_1 = p_1'', \qquad (11)$$

$$p_1 = m_1, \qquad (12)$$

whereas the boundary conditions remain Eqs. (9) or (10) for the blocking or adsorbing electrodes, respectively. Equations (11) are equations of diffusion, widely considered in supported systems [17]. As is evident, solutions of Eqs. (11) and (12) with the boundary conditions Eqs. (9) or (10) are the trivial ones $p_1 = m_1 = 0$, for $E_1 \neq 0$. Probably, this means that the equation $p_1 = m_1$ is valid only to some degree of approximation, not discussed in Ref. [3]. We note also that, in all the analysis presented in Ref. [3], $p_1 = -m_1$ as follows from Eqs. (17)–(22) or Eqs. (33)–(38) of Ref. [3].

By means of standard calculations, the current in the cell is given by Eq. (23) of Ref. [3], that is

$$j_1(x) = i\omega\varepsilon_0\varepsilon_s E_1 + q\left\{2\mu c_0 E_1 - D\left(\frac{dp_1}{dx} - \frac{dn_1}{dx}\right)\right\}, \tag{13}$$

where we have taken into account that $E(t) = E_1 \exp(i\omega t)$ and $E_1 = V_1/d$. Equation (13) can be rewritten as

$$j_1(x) = i\omega\varepsilon_0\varepsilon_s E_1 + j_{p_1} + j_{m_1}, \qquad (14)$$

if Eqs. (15) and (16) of Ref. [3] are taken into account. The current in the external circuit is simply given by

$$J_1 = j_1(d) = i\omega\varepsilon_0\varepsilon_s E_1 + j_{p_1}(d) + j_{m_1}(d). \qquad (15)$$

Let us consider first the case where the electrodes are blocking, discussed in Sec. II A of Ref. [3]. In this case, from Eq. (15), for the blocking character of the electrodes, we obtain

$$J_1 = j_1(d) = i\omega\varepsilon_0\varepsilon_s E_1 = i\omega\varepsilon_0\varepsilon_s \frac{V_1}{d}, \qquad (16)$$

as expected since, in this case, the current in the external circuit is just due to the displacement current. From this equation, it follows that, in the framework of Ref. [3], the admittance per unit area of the cell is simply

$$Y_1 = \frac{J_1}{V_1} = i\omega\frac{\varepsilon_0\varepsilon_s}{d}, \qquad (17)$$

i.e., the cell behaves as a true condenser. Equation (17) is different from Eq. (25) reported in Ref. [3]. Note that to evaluate the current in the external circuit by means of

$$J_1 = \frac{1}{d}\int_0^d j_1 dx, \qquad (18)$$

as performed in Ref. [3] is correct only if $j_1(x)$ is position independent [18], that is not the case in the framework considered in Ref. [3]. In fact, from Eq. (13), we obtain

$$\frac{dj_1}{dx} = -i\omega q[p_1(x) - n_1(x)] = -2i\omega q p_1(z), \qquad (19)$$

that is not identically zero, as required for the application of Eq. (18).

Let us consider, finally, the case where the electrodes are adsorbing. According to the calculation reported in Ref. [3], the admittance per unit area is given by

$$Y_{1S} = \frac{2q\mu c_0 + i\omega\varepsilon_0\varepsilon_s}{d} \\ -2\frac{qD}{dV_1}\{A_{ap}(e^{Zd} - 1) + B_{ap}(e^{-Zd} - 1)\}, \qquad (20)$$

where $Z = \sqrt{i\omega/D}$, that coincides with Eq. (39) of Ref. [3] if one takes into account that, as follows from Eqs. (35)–(38) of Ref. [3], $A_{ap} = -A_{an}$ and $B_{ap} = -B_{an}$. Equation (20) has been obtained evaluating the electric current in the external circuit by means of Eq. (18), that is not correct. If the current is evaluated by means of (15) with the expressions (33) and (34) taking into account (35)–(38) of Ref. [3], we get

$$Y_{1C} = \frac{2q\mu c_0 + i\omega\varepsilon_0\varepsilon_s}{d} \\ -2\frac{qDZ}{V_1}\{A_{ap}(e^{Zd} - 1) + B_{ap}(e^{-Zd} - 1)\}, \qquad (21)$$

that differs from Eq. (20) in the second term, where the coefficient $2qD/(dV_1)$ is replaced by $2qDZ/V_1$. Taking into account that $Z = \sqrt{i\omega/D}$, we can conclude that the disagreement between $Y_{1S}$ and $Y_{1C}$ depends on the frequency.

In Fig. 1, we compare the real $\varepsilon'$ [Fig. 1(a)], and imaginary $\varepsilon''$ [Fig. 1(b)] parts of the dielectric constant derived in the framework of the model proposed in Ref. [3] when the current in the external circuit is determined by Eq. (15) or by Eq. (18).
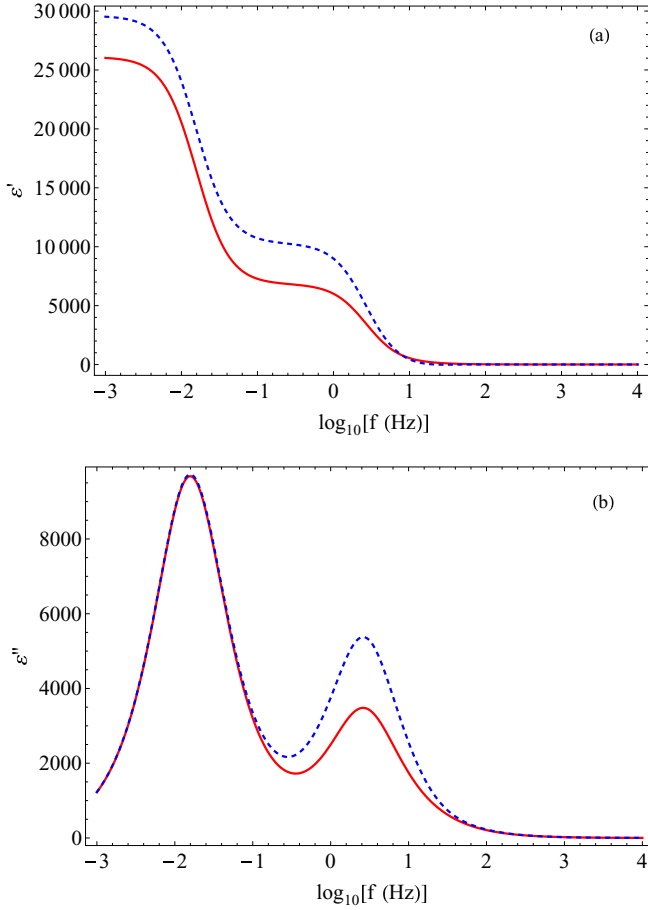
FIG. 1. (Color online) Spectrum of (a) $\varepsilon'$ and of (b) $\varepsilon''$, determined in the framework of the model proposed in Ref. [3] using for the admittance expression $Y_{1S}$ (red) and expression $Y_{1C}$ (blue dashed line) in the presence of adsorption from the electrodes. The parameters for the numerical calculations are reported in the text.

We limit our comparison to the case of adsorbing electrodes. For the numerical calculations, we assume $V_1 = 0.01$ V that the ions are monovalent ($q = 1.6 \times 10^{-19}$ A s) with a diffusion coefficient $D = 8.2 \times 10^{-10}$ m$^2$/s in chlorobenzene, whose dielectric constant is $\varepsilon = 5.6 \times \varepsilon_0$. The mobility of the ions is evaluated by means of $\mu = (q/K_B T)D$. The thickness of the sample is $d = 22$ μm, $c_0 = 1.2 \times 10^{20}$ m$^{-3}$, $\xi_\infty = 10^{-6}$ m/s, and $\tau = 10$ s as in Ref. [3]. As is evident from Fig. 1, the frequency dependencies for $\varepsilon'$ and $\varepsilon''$ are the same, but the numerical values differ in a frequency range of 0.1–10 Hz. The numerical disagreement strongly depends on $\xi_\infty$ and $\tau$. We note, in particular, that, if the current is correctly determined, $\varepsilon'$ becomes negative between 10 and 100 Hz, which is, apparently, absurd.

Finally, note that the assumption of full dissociation in Ref. [3] is questionable. In fact, the effect of recombination is important when the electrostatic energy between two ions is comparable with the thermal energy [19]. The limit density for which this hypothesis works well can be roughly determined as follows. Let $r$ be the average distance between two ions of opposite sign. The electrostatic energy, responsible for the recombination, is $U_e = (1/4\pi\varepsilon)q^2/r$ in the SI. The thermal energy of the ion, assumed pointlike, is $U_t = (3/2)K_B T$.

When $U_e \sim U_t$, there is recombination. The distance $r$ for which the recombination takes place is fixed by $U_e = U_t$ and is known as the radius of Bjerrum. For a bulk density of ions $c_0$, the average distance between the ions is on the order of $\ell = c_0^{-1/3}$, assuming that the ions form a cubic lattice of parameter $\ell$. If $\varepsilon \sim 5.6 \times \varepsilon_0$, $q = 1.6 \times 10^{-19}$ A s, and $c_0 \sim 5.6 \times 10^{22}$ [3], we obtain $\ell = 2.6 \times 10^{-8}$ m and $U_e = 1.6 \times 10^{-21}$ J. Since $U_t \sim 6 \times 10^{-21}$ J, it follows that $U_e$ is comparable with $U_t$ and the hypothesis of full dissociation has to be assumed with precaution. In this situation, the problem of the response of the cell to an external excitation should be faced according to the lines discussed in Ref. [20].

In Ref. [3], just before Eq. (33), the author states that "the analytical formula by Barbero [11] does not take account of the influence of external charges on the internal field formation, and thus, it cannot be used for the analysis of practical experiment data." This statement is not correct for the following reason. In Ref. [11], the electric field has been evaluated solving the full PNP model, taking into account not only the continuity equations, but also the Poisson equation for the actual potential across the sample. In Eq. (14) of Ref. [11], the two contributions depend on the distribution of the ionic charge as it follows from the following Eqs. (15) of the same reference, contrary to the analysis presented in Ref. [3] where the field is assumed independent of the ionic distribution. In Ref. [11], also the electrical current is evaluated in a correct manner. It is possible to verify this in the following simple manner. Let us assume that the electrodes are adsorbing. We indicate, by $\sigma_p$ and $\sigma_m$, the surface density of adsorbed positive and negative ions on the electrode at $x = d$ due to the external voltage of amplitude $V_1$. In this case, the boundary conditions at $x = d$ for the current densities of particles are $j_p = d\sigma_p/dt$ and $j_m = d\sigma_m/dt$ for the positive and negative ions, respectively. It follows that the electric current density on the electrode is

$$j = \varepsilon \left( \frac{\partial E}{\partial t} \right)_d + q(j_p - j_m) = \varepsilon \left( \frac{\partial E}{\partial t} \right)_d + q \left( \frac{d\sigma_p}{dt} - \frac{d\sigma_m}{dt} \right),$$
(22)

that can be rewritten as

$$j = \frac{\partial}{\partial t} \{\varepsilon E(d,t) + q(\sigma_p - \sigma_m)t\}.$$
(23)

Since the surface electric field is

$$E(d,t) = q\{\Sigma(t) - [\sigma_p(t) - \sigma_m(t)]\},$$
(24)

where $q\Sigma(t)$ is the surface charge density sent by the external power supply to fix the difference of potential $\Delta V(t) = V_1 \exp(i\omega t)$ to the cell, we can finally set Eq. (23) in the form

$$j = q \frac{d\Sigma}{dt},$$
(25)

as reported in Ref. [11]. It follows that the criticism on Ref. [11] in Ref. [3] is not pertinent.

We have shown that the assumption of uniform electric field in Ref. [3] across the sample is far from being realistic and pointed out that, in the framework of the model proposed in Ref. [3], the electrical current used to determine the admittance of the cell is not correctly evaluated. We agree with Sawada that probably the standard PNP model is unable to justify the

experimental data published in Refs. [1–3] and it has to be generalized. However, even if the model proposed in Ref. [3] is able to fit the experimental data with a reasonable value of the diffusion coefficient assumed on the order of $D \sim 10^{-9}$ m$^2$/s, it seems to us that it is not physically based and contains inconsistencies. We note that the interpretation of diffusion coefficients fitted to polarization models requires care as is underlined in Ref. [7] that the diffusion coefficient, determined by means of electrode polarization, can be up to four orders of magnitude higher than the values obtained by NMR.

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