On the equivalence between specific adsorption and kinetic equation descriptions of the admittance response in electrolytic cells

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The response of an electrolytic cell, in the shape of a slab, is analyzed in the framework of the Poisson-Nernst-Planck model in the limit of full dissociation. Two different types of boundary conditions on the electrodes are compared. One type describes the exchange of charges between the volume and the external circuit, in the form originally proposed by Chang and Jaffé and later extended to include specific adsorption, where the surface current density is proportional to the variation of the surface bulk density of ions with respect to the value of equilibrium. The other one describes the surface adsorption, in the limit of Langmuir. We show that in the simple case where the ions dissolved in the insulating liquid are identical in all the aspects, except for the sign of the charge, the two models are equivalent only if the phenomenological parameter entering the boundary condition of the Chang-Jaffé model, κ, is frequency dependent, and related to the adsorption coefficient, k_a, in the form $\kappa = i\omega\tau/(1 + i\omega\tau)k_a$, where τ is the desorption time and ω the circular frequency of the applied voltage, as proposed long ago by Macdonald. © *2013 American Institute of Physics.* [http://dx.doi.org/10.1063/1.4794689]

I. INTRODUCTION

The selective adsorption of ions occurring at the electrodes has been invoked as one of the relevant processes to describe the role of the mobile charges on the admittance or immittance response of typical electrolytic cells.[1,2] The small-signal Poisson-Nernst-Planck (PNP) diffusion model for the analysis of impedance spectroscopy (IS) data is particularly important in this context because when one utilizes it to analyze immittance data, preferably using full complex nonlinear least squares (CNLS) fitting, as in the LEVMW computer program,[3–5] it can lead to estimates of many more physically relevant electrical parameters than can any other available IS model.

Although the PNP diffusion model is a mean-field, conductive-system, effective-medium continuum one that considers point charges inside a non-dispersive dielectric medium, it may nevertheless well fit some situations involving charges hopping in a diffusive manner between sites separated by random barriers. The PNP model considers a neutral species that can dissociate into positive and negative charges of arbitrary mobilities and equal concentrations. Thus, fits of experimental data with this model can lead to estimates of the neutral-species concentration, the concentration of the mobile positive and negative charges, their mobilities and diffusion constants, their dissociation and recombination parameters, and reaction and adsorption parameters for each of the two species of mobile charges, as well as a fractional-exponent parameter when the model is generalized to include anomalous diffusion. Here, however, we primarily consider only adsorption processes, not sequential specific adsorption and Faradaic reactions at electrodes.

In the framework of the PNP model, the case of pure-adsorption boundary conditions (i.e., adsorbed species not reacting after adsorption at electrodes) has been considered in detail long ago by Macdonald and co-authors.[6–13] The original 1952 reaction-only Chang-Jaffé boundary conditions[14] were extended in these papers to complex form in order to include adsorption and were shown to be consistent with the basic Butler-Volmer ones and with the early Langmuir adsorption isotherm. The final complex form of the extended Chang-Jaffé parameters (up to three for charges of each sign) that included both adsorption and sequential reactions appears in Ref. 11. These boundary conditions are such that the ionic current on the electrodes is proportional to the variation of the bulk density of ions in front of the electrodes. In a recent paper by some of us,[15] adsorption boundary conditions have been analyzed in the same framework, but from a different perspective.

In Ref. 15, the adsorption-desorption phenomenon has been incorporated in the boundary conditions by means of a kinetic equation describing a chemical reaction of the first kind (Langmuir approximation) at the interface liquid medium—electrodes. Further, the conservation of the number of particles in the entire bulk plus the electrode system was

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imposed,[16,17] an approximation certainly valid in the limit of weak adsorption and no evolution processes. Although the adsorption boundary equations used in Ref. 15 were overtly different from those of Ref. 11, later CNLS fitting of all the theoretical responses presented in Ref. 15 with the PNP model available in the LEVMW computer program that includes the full extended Chang-Jaffé boundary conditions led to exact numerical agreement, including identical adsorption results. Motivated by the exact numeric agreement between the two approaches, here we consider a typical electrolytic system (e.g., a liquid medium) in which positive and negative species of mobile charges are present in order to show analytically how to connect the predictions of the earlier PNP models with that of the recent PNP model of Ref. 15. Indeed, by means of simple arguments, we demonstrate that the two models are fully equivalent, confirming that the extended Chang-Jaffé adsorption parameter involves a specific frequency dependence that is a direct consequence of the Langmuir approximation used for the balance equation in the time-domain.

II. PNP MODEL

A. Fundamental equations

In our analysis we assume that the impurities dissolved in the liquid are fully dissociated. This permits us to consider here the same set of fundamental equations presented in Ref. 11, for the case in which the association-dissociation processes are not taken into account. In this framework, we consider a typical one-dimensional system of thickness d whose bulk densities of the mobile charges are represented by $n_+(z, t)$ (positive) and $n_-(z, t)$ (negative), with z being the coordinate normal to the flat electrodes placed at the positions $z = \pm d/2$ of a Cartesian system. The continuity equations may be written as

$$\frac{\partial n_+}{\partial t} = -\frac{\partial j_+}{\partial t} \quad \text{and} \quad \frac{\partial n_-}{\partial t} = -\frac{\partial j_-}{\partial t}, \quad (1)$$

where

$$j_+ = -D_+ \frac{\partial n_+}{\partial z} - \frac{q\, D_+}{K_B T} \frac{\partial V}{\partial z} n_+ \quad \text{and}$$

$$j_- = -D_- \frac{\partial n_-}{\partial z} + \frac{q\, D_-}{K_B T} \frac{\partial V}{\partial z} n_- \quad (2)$$

are the current densities of positive and negative ions. In these equations, $D_\pm$ are the diffusion coefficients for both species of ions, q is the ion charge, K_B is the Boltzmann constant, and T is the absolute temperature. To save space, in the above expressions, we have used a simplified notation, i.e., $n_\pm = n_\pm(z, t)$ and $j_\pm = j_\pm(z, t)$. We also make the usual assumptions that dielectric constant, ϵ, diffusion coefficients, and mobilities, given by Einstein relation, $\mu_\pm = qD_\pm/K_B T$, are all position and field independent.

B. Chang-Jaffé boundary conditions

The original Chang-Jaffé electrode-reaction boundary conditions were introduced by Friauf[18] to investigate partial-blocking effects. The extended Chang-Jaffé boundary conditions have been considered subsequently[19] and generalized

to include specific ion adsorption a few years later[11] (for a detailed discussion on boundary conditions see Ref. 20). The problem will be solved here by using the following version of the Chang-Jaffé boundary conditions, as expressed in Eqs. (10)–(13) of Ref. 11:

$$j_+|_{z=\pm d/2} = \kappa_+ (n_+ - N_e^+)_{z=\pm d/2} \quad \text{and}$$

$$j_-|_{z=\pm d/2} = \kappa_- (n_- - N_e^-)_{z=\pm d/2}, \quad (3)$$

but, hereafter, we assume that $N_e^+ = N_e^- = N_e$ and $\kappa_+ = \kappa_- = \kappa$, i.e., there is only a single Chang-Jaffé parameter, represented by κ. In the linear approximation (small-signal ac response), when the applied potential has the form $V = V_0 e^{i\omega t}$, where V_0 is the amplitude and $\omega = 2\pi f$ is the radial frequency, one can write

$$n_+(z, t) = N + \eta_+(z)e^{i\omega t} \quad \text{and} \quad n_-(z, t) = N + \eta_-(z)e^{i\omega t}. \quad (4)$$

Since $n_+ - n_- = (\eta_+ - \eta_-)e^{i\omega t}$, if we assume furthermore that $D_+ = D_- = D$, by means of Eqs. (1) and (2), one may easily find:

$$\frac{\partial}{\partial t}(n_+ - n_-) = D\frac{\partial^2}{\partial z^2}(n_+ - n_-) + \frac{2Nq}{K_B T}\frac{\partial^2 V}{\partial z^2}, \quad (5)$$

where the profile of the electrical potential, $V(z, t)$, is governed by the Poisson's equation in the form:

$$\frac{\partial^2 V}{\partial z^2} = -\frac{q}{\varepsilon}(n_+ - n_-). \quad (6)$$

If we now introduce the quantity $\Psi(z, t) = [\eta_+(z) - \eta_-(z)]e^{i\omega t} = \psi(z)e^{i\omega t}$, Eq. (5) becomes

$$\frac{d^2\psi}{dz^2} - \left(\frac{1}{\Lambda^2} + i\frac{\omega}{D}\right)\psi = 0, \quad (7)$$

where Λ is the Debye screening length defined by

$$\Lambda^2 = \frac{\varepsilon K_B T}{2Nq^2}. \quad (8)$$

As usual, we define $\beta^2 = 1/\Lambda^2 + i\omega/D$, and search for solutions in the form $\psi(z) = A\sinh(\beta z) + B\cosh(\beta z)$, and $V(z, t) = \phi(z)e^{i\omega t}$. Since the applied potential is such that $V(d/2, t) = -V(-d/2, t)$, it follows that $\phi(z) = -\phi(-z)$. By rewriting Poisson's equation in the form

$$\frac{d^2\phi}{dz^2} = -\frac{q}{\varepsilon}\psi, \quad (9)$$

we deduce that $\psi(z) = -\psi(-z)$. Thus, $B = 0$ and we easily obtain

$$\phi(z) = -\frac{qA}{\varepsilon\beta^2}\sinh(\beta z) + Cz. \quad (10)$$

Let us now rewrite the boundary conditions (3) in terms of a subtraction between two equations, in a form that will reveal to be useful later, namely,

$$(j_+ - j_-)_{z=\pm d/2} = \pm\kappa (n_+ - n_-)_{z=\pm d/2}. \quad (11)$$

Using these boundary conditions with the requirement that $\phi(d/2) = V_0/2$, simple calculations yield the integration constants A and C, whose explicit forms will be omitted here to save space, which permits to obtain the exact electric field profile across the sample. Once this profile is achieved, the next step needed to obtain analytical expressions for the admittance $Y = I/V$ is to calculate the current, I, when the

electrodes have the area S and the electric field is given by $E(z, t) = -\partial V(z, t)/\partial z$. One can write

$$I = \left[qS(j_+ - j_-) + S\varepsilon \frac{d}{dt} E \right]_{z=d/2},$$

which, after some calculations, eventually yield for the electrical impedance $Z = 1/Y = V_0/I e^{i\omega t}$:

$$Z = R_\infty \frac{M\Omega\sqrt{1 + i\Omega} - i\left[1 + MH(1 + i\Omega)\right]\tanh\left(M\sqrt{1 + i\Omega}\right)}{M(1 + i\Omega)\left[\Omega\sqrt{1 + i\Omega} - iH(1 + i\Omega)\tanh\left(M\sqrt{1 + i\Omega}\right)\right]}, \tag{12}$$

where, for comparative purposes, we have used the notation of Ref. 21, i.e.,

$$R_\infty = \frac{\Lambda^2 d}{\varepsilon SD}, \quad H = \frac{\kappa\Lambda}{D}, \quad M = \frac{d}{2\Lambda}, \quad \Omega = \frac{\omega}{\omega_D}, \quad \text{and}$$

$$\omega_D = \frac{D}{\Lambda^2}.$$

It is noteworthy that Eq. (12) coincides strictly with Eq. (10) of Ref. 21, obtained in the hypothesis of one mobile charge, i.e., $D_+ = D \neq 0$ and $D_- = 0$. However, we notice that in Ref. 21 one has

$$\Lambda^2 = \frac{\varepsilon K_B T}{N_0 q}, \tag{13}$$

which is different from (8) just by a factor 2, when we identify $N = N_0$. Thus, the final formulae for Z here and in Ref. 21 are the same, but the Debye screening lengths differ by the presence of a factor of 2 in the denominator because of the difference between one-mobile and two-mobile situations. The ambiguity between one-mobile response and two-mobile response with equal mobilities of the positive and negative charges has been discussed in detail recently in Ref. 22.

C. Adsorption-desorption process: Langmuir's approximation

One of the simplest ways to incorporate the adsorption-desorption process to the description of the immittance response of the cell is to express the boundary conditions in terms of a kinetic equation (Langmuir's approximation) in the form:

$$\frac{d\sigma_\pm(t)}{dt} = k_a^\pm n_\pm(d/2, t) - \frac{1}{\tau}\sigma_\pm(t), \tag{14}$$

in which $k_a^\pm$ and $\tau_\pm$ are parameters describing the adsorption phenomenon for each species of ions. See, for example, the earlier kinetic-equation approaches implemented in Ref. 9. Equation (14) simply states that the time variation of the surface density of adsorbed particles $\sigma_\pm(t)$ depends on the bulk density of particles just in front of the adsorbing surface, located, for instance, at $z = d/2$, and on the surface density of particles already adsorbed. The parameter $\tau_\pm$ has the di-

mension of time, whereas the $k_a^\pm$ parameters have the dimension of a length/time. Consequently, when the adsorption phenomenon is present, from the kinetic equation it follows that there is an intrinsic thickness $k_a^\pm\tau_\pm$. Henceforth, we assume that $k_a^+ = k_a^- = k_a$ and $\tau_\pm = \tau$ in such a manner that in the absence of an external electric field the liquid is locally neutral, and the surface densities of positive and negative adsorbed ions are the same. In this framework, for $V_0 = 0$ the electric field across the sample is identically zero. Thus, to connect the preceding calculations with the adsorption-desorption process faced by means of the usual kinetic equation, we consider the following boundary conditions[2]

$$j_+|_{z=\pm d/2} = \pm\frac{d\sigma_+}{dt}|_{z=\pm d/2} \quad \text{and}$$

$$j_-|_{z=\pm d/2} = \pm\frac{d\sigma_-}{dt}|_{z=\pm d/2}, \tag{15}$$

in such a way that by subtracting one from the other we obtain

$$(j_+ - j_-)_{z=\pm d/2} = \pm\frac{d}{dt}(\sigma_+ - \sigma_-)_{z=\pm d/2}. \tag{16}$$

In the linear approximation,[2]

$$\sigma_+ = \sigma + s_+ e^{i\omega t} \quad \text{and} \quad \sigma_- = \sigma + s_- e^{i\omega t} \tag{17}$$

and Eq. (16) can be rewritten as

$$(j_+ - j_-)_{z=\pm d/2} = \pm i\omega(s_+ - s_-)e^{i\omega t} = \pm i\omega\Delta s e^{i\omega t}, \tag{18}$$

with $\Delta s = s_+ - s_-$. However, since in our framework $k_a^+ = k_a^- = k_a$ and $\tau_\pm = \tau$, i.e., the adsorption parameters are the same for positive and negative charges, we may rewrite the kinetic equations in the form:

$$\frac{d\sigma_\pm}{dt} + \frac{1}{\tau}\sigma_\pm = k_a n_\pm \tag{19}$$

in such a manner that, again by subtraction, one obtains

$$\frac{d}{dt}(\sigma_+ - \sigma_-) + \frac{1}{\tau}(\sigma_+ - \sigma_-) = k_a(n_+ - n_-).$$

Using Eq. (17), one easily obtains

$$\Delta s = \frac{k_a \tau}{1 + i\omega\tau}\,\psi. \qquad (20)$$

Thus, Eq. (18) finally becomes

$$(j_+ - j_-)_{z=\pm d/2} = \pm \frac{i\omega\tau}{1 + i\omega\tau} k_a \psi e^{i\omega t} \qquad (21)$$

and has to be compared with Eq. (11) for the boundary conditions involving the Chang-Jaffé prescription. They are equivalent if

$$\kappa = \frac{i\omega\tau}{1 + i\omega\tau}\,k_a. \qquad (22)$$

Indeed this is exactly the case for the adsorption-only version of the earlier full extended Chang-Jaffé result of Eq. (B38) of Ref. 11, thereby proving the consistency of the present approach with the earlier one.

As is evident from Eq. (22), for real frequency-independent values of the adsorption coefficient k_a and desorption time τ, a complex, frequency-dependent phenomenological parameter κ is required to extend the original Chang-Jaffé boundary conditions to include specific adsorption. This is not surprising because when combining the Chang-Jaffé and Langmuir models, we equate their expressions for the electrical impedance. From Eq. (22) it follows that the real and imaginary parts of $\kappa = \kappa_r + i\kappa_i$ are given by

$$\kappa_r = \frac{(\omega\tau)^2}{1 + (\omega\tau)^2}\,k_a \quad \text{and} \quad \kappa_i = \frac{\omega\tau}{1 + (\omega\tau)^2}\,k_a.$$

In the limit of $\omega\tau \to 0$, $\kappa_r \to 0$ and $\kappa_i \to (\omega\tau)k_a$. This indicates that in the dc limit the extended Chang-Jaffé boundary conditions for adsorption-only lead to complete blocking. For small $\omega\tau$, κ is imaginary, showing that the current across the electrodes is in quadrature with the bulk density variation of the ions just in front of the electrode itself. In the opposite limit, where $\omega\tau \to \infty$, we get $\kappa_r \to k_a$ and $\kappa_i \to 0$. In this limit there exists a one-to-one correspondence between the two models. However, in this limit the effect of the non-blocking character of the electrodes is not visible because the response of the cell is then mainly due to that of the bulk of the system.

Simple calculations show that κ_r is a monotonic function of $\omega\tau$ increasing from 0 to k_a, whereas κ_i presents a well defined maximum for $\omega\tau = 1$, where its value is $k_a/2$, and it tends to 0 for $\omega\tau \to 0$ and $\omega\tau \to \infty$. These results are the expected ones in view of the simple Debye behavior of these two quantities.

III. CONCLUSIONS

We have considered a typical electrolytic system in which mobile charges of both signs are present in the framework of the small-signal PNP diffusion model usually employed for the analysis of impedance spectroscopy data. We have shown how to analytically connect the predictions of earlier PNP models, based on Chang-Jaffé boundary conditions in the frequency domain that agree with the basic Butler-Volmer ones, and, for adsorption, have been shown to encompass Langmuir behavior as well, with a recently published PNP model, using a balance equation to describe adsorption-desorption pro-

cesses at the interface. We have demonstrated here that the two models are fully equivalent only if the phenomenological parameter entering the boundary condition of the Chang-Jaffé model, κ, is frequency dependent, and related to the adsorption coefficient, k_a, according to expression (22). This happens because the earlier extended Chang-Jaffé adsorption-reaction parameters properly include exactly the specific frequency dependence that is a direct consequence of the Langmuir approximation used for the kinetic equation written in the time-domain.

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