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Poisson–Nernst–Planck model with Chang-Jaffe, diffusion, and ohmic boundary conditions

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Abstract
Using the linear Poisson–Nernst–Planck impedance-response continuum model, we investigate the possible equivalences of three different types of boundary conditions previously proposed to model the electrode behavior of an electrolytic cell in the shape of a slab. We show analytically that the boundary conditions proposed long ago by Chang-Jaffe are fully equivalent to the ohmic boundary conditions only if the positive and negative ions have the same mobility, or when only ions of a single polarity are mobile. In the case where the ions have different and non-zero mobilities, we fit exact impedance spectra created for ohmic boundary conditions by using the Chang-Jaffe Poisson–Nernst–Planck response model, one that is dominated by diffusion effects. These fits yield conditions for essentially exact or approximate numerical correspondence for the complex impedance between the two models even in the unequal mobility case. Finally, diffusion type boundary conditions are shown to be fully equivalent to the ohmic one. Some limiting cases of the model parameters are investigated.

Keywords: impedance spectroscopy, non-blocking electrodes, real electrodes, boundary conditions for the PNP model

(Some figures may appear in colour only in the online journal)

I. Introduction

The impedance spectroscopy technique is widely used in the dielectric characterization of solid and liquids [1]. According to this technique a simple harmonic difference of potential, $\Delta V(t) = V_0 \exp(\mathrm{i}\omega t)$, of small amplitude V_0 is applied to the sample of a well defined geometry, and the electric impedance Z of the sample is measured versus the frequency $f = \omega/(2\pi)$ of the applied voltage. From the spectra of the real, $R = \Re[Z]$, and imaginary, $X = \Im[Z]$, parts of the impedance it is possible to test models proposed to describe the electric response of the sample to external electric stimulus. The analysis performed in this manner is called at the 'impedance level'. In some situations is more convenient to consider the admittance of the sample, defined by $Y = 1/Z$, and measure $G = \Re[Y]$, and $B = \Im[Y]$. This kind of analysis is called at the 'immittance level'. Of course for a good conducting medium, the impedance level is indicated, whereas for a good insulator the admittance level is more suitable. Very often the analysis is performed at the 'dielectric level', where the spectra of the real, ε', and the imaginary, ε'', parts of the complex dielectric constant, ε, are related to the complex capacitance of the sample.

The models proposed to describe the response of a medium to an external electric field depend on the material under investigation. We are interested in the electric response of insulators containing ionic impurities. As it is well known, an insulator is a medium through which no steady conduction current can flow when it is submitted to an external electric field. If the external voltage is simply harmonic the impedance of the sample is of capacitive type. However, true insulator behavior is never observed for the ionic impurities present in it, are responsible for a transient current when a dc field is applied. In the following we are interested in the influence of the ions on the electrical response of an insulator material submitted to a simple periodic external voltage due to a power supply. We assume that the frequency range of the external difference of potential is few MHz, in such a manner that the medium could be considered non-dispersive. From this assumption it follows that the dispersion of the sample is due only to the ions dissolved in the medium under investigation. The model describing the electric response of the sample has to take into account the contribution of the ions to the current, I, flowing in the external circuit, which is measured to determine the impedance of the cell by means of $Z = \Delta V(t)/I$. The presence of the electric field is responsible for a redistribution of the ions dissolved in the medium and supposed free to move, whose distribution is assumed uniform in the absence of the external electric field. The model proposed in the past for the description of an insulating medium containing ions is based on the equations of continuity for the positive and negative ions, related to the conservation of ions, and to the equation of Poisson, connecting the ionic charge density with the actual electric potential. In the case in which there is just a group of positive an negative ions, the equations of the model are three partial differential equations valid in the bulk. According to this model, the medium is described by the dielectric constant, and the interaction of the ions with the medium by means of the diffusion coefficients only, if the validity of Einstein's relation between the electric mobility and diffusion coefficient is considered valid. The partial differential equations valid in the bulk have to be solved with the proper boundary conditions on the electric potential and the ionic current densities on the electrodes.

The model described above is known as Poisson–Nernst–Planck model (PNP), and it was first fully expressed for completely blocking electrodes in 1953 [2] and recently reconsidered by [3–9] for its practical importance [10–17]. The Chang-Jaffe (CJ) boundary conditions [18] were soon incorporated into the PNP model, leading to the CJPNP one. Such extension took account of the possible presence of electrode reactions involving mobile charges over the span of none (full blocking), partially blocking, to transparent (no blocking). Further work led to the ECJPNP model which included electrode adsorption effects [19], but here only the CJPNP model is used to compare with other PNP models incorporating ohmic boundary conditions (OBC), and other related BCs [20, 21]. Useful discussions on BCs and illustrations of possible CJPNP responses appears in [22, 23].

Many different boundary conditions have been proposed to model real electrodes, for the theoretical description of an electrolytic cell, and for the analysis of experimental data. When chemical reactions occur at the electrodes, charge transport takes place and a conduction current appears. The dielectric response of a cell considerably changes with the type of the electrodes, especially at low frequencies where mobile ions contribute to the effective dielectric constant by formation of a surface double layer. Similar responses often appear for different types of BCs, and it has been formally demonstrated that in some cases different models are equivalent. For example, when the ions have the same mobility, equivalence was shown between the adsorption-only ECJPNP Chang-Jaffe BC and the adsorption in the limit of Langmuir approximation [24]. In the case where the ions of only one sign are mobile, the CJBCs are also equivalent to the ohmic BCs (OBCs) as has been shown in [21, 23].

In the present paper we consider the general case of ions with different mobilities in an electrolytic cell with electrodes that have different affinities for cations and anions. Previous studies, cited before, investigate cases where either ions of both signs have the same mobility or ions of only one sign are mobile while ions of the opposite sign are immobile. Our aim is to investigate if for partially blocking electrodes described by three different models there is any equivalence between the models. The BCs we study are (i) the ohmic BCs (OBCs), the Chang-Jaffe BCs (CJBCs), and the diffusion type BCs (DBCs) [25]. Our investigation is done in the framework of the Poisson–Nernst–Planck model where the distribution of ions due to an external electric field is described by the equations of continuity for the cations and anions, and the equation of Poisson that relates the effective electric field to the bulk density of ionic charge [2]. Our paper is organized as follows: in section II, we briefly recall the PNP model and its fundamental equations and give its general solution in the case of a cell in the form of a slab. Different kinds of BCs are presented in section III, and in section IV the problem of analytical equivalence is investigated. In section V, we study the problem of numerical equivalence. Finally, section VI is devoted to conclusions.

II. Bulk equations

We consider an electrolytic cell composed by an isotropic dielectric liquid between two flat electrodes in parallel position and located at $z = \pm L/2$. The electrolytic solution contains two types of ions, p, n, with charge $\pm q$ and mobilities μ_p and μ_n for cations and anions respectively. The bulk continuity and Poisson equations that describe the PNP system are written as [22]

$$\begin{aligned}
\frac{\partial N_p}{\partial t} &= -\nabla \cdot \mathbf{j}_p = D_p \nabla \cdot \left(\nabla N_p - \frac{\mu_p}{D_p} N_p \mathbf{E} \right) \\
\frac{\partial N_n}{\partial t} &= -\nabla \cdot \mathbf{j}_n = D_n \nabla \cdot \left(\nabla N_n + \frac{\mu_n}{D_n} N_n \mathbf{E} \right) \\
\nabla \cdot \mathbf{E} &= q\, \frac{N_p - N_n}{\varepsilon_s},
\end{aligned} \tag{1}$$

where ε_s is the dielectric permittivity of the solvent, and $N_a(\mathbf{r}t)$, with $a = p, n$, are the local densities of ions. D_a are the diffusion coefficients of the ions which are related with mobilities via the Einstein–Smoluchowski relations: $\mu_a / D_a = q / k_B T$ [26], where k_B is the Boltzmann constant and T the temperature. In the present analysis, we assume that the dissolved impurities in the liquid are completely dissociated and therefore association-dissociation effects are not considered. The ions are supposed point-like and the system as one-dimensional. The electrodes are identical.

Henceforth, we introduce the following reduced quantities

$$U_p = \frac{N_p - N_0}{N_0}, \quad U_n = \frac{N_n - N_0}{N_0}, \quad \text{and} \quad U_v = \frac{qV}{k_B T} = \frac{V}{V_{th}}, \tag{2}$$

where N_0 is the bulk density of ions at thermodynamical equilibrium, V_{th} is the thermal voltage, and V the applied electric potential supposed of small enough amplitude to justify the linear treatment of the problem [27]. In the following we limit our analysis to the case where the applied voltage is $\Delta V(t) = V(L/2, t) - V(-L/2, t) = V_0 \exp(i\omega t)$, or in reduced form $\Delta U_v(t) = U_v(L/2, t) - U_v(-L/2, t) = u_0 \exp(i\omega t)$, where ω is the circular frequency of the applied voltage.

In the linear version of the PNP model U_p, U_n and U_v are small quantities, of the first order, that can be decomposed as $U_p(z, t) = u_p(z) \exp(i\omega t)$, $U_n(z, t) = u_n(z) \exp(i\omega t)$, and $U_v(z, t) = u_v(z) \exp(i\omega t)$. In this framework ε_s and D_a are position independent [28, 29]. By means of a standard calculation reported in [30, 31], one obtains the following expressions for the z dependencies of the charge and electrical potential profile in the cell

$$u_p(z) = C_1 \sinh(\nu_1 z) + C_2 \sinh(\nu_2 z), \tag{3}$$

$$u_n(z) = k_1 C_1 \sinh(\nu_1 z) + k_2 C_2 \sinh(\nu_2 z), \tag{4}$$

$$u_v(z) = -\frac{1}{2L_D^2}\left\{\frac{1-k_1}{\nu_1^2} C_1 \sinh(\nu_1 z) + \frac{1-k_2}{\nu_2^2} C_2 \sinh(\nu_2 z)\right\} + Az, \tag{5}$$

where $L_D = \sqrt{\varepsilon_s k_B T/(2N_0 q^2)}$ is Debye's screening length and $\nu_{1,2}, k_{1,2}$ are given in appendix A. The integrations constants, C_1, C_2 and A have to be determined by means of the boundary conditions imposed on the electric potential, and on the ionic current densities at the electrodes.

III. Boundary conditions

III.A. BCs on the potential

The BCs concerning the electric potential related to the external power supply are

$$u_v(\pm L/2, t) = \pm \frac{u_0}{2} e^{i\omega t}. \tag{6}$$

These BCs on the potential are the same for all the three types of partially blocking electrodes we consider.

III.B. BCs on the ionic currents

Our goal is to investigate the equivalence between a few models proposed to describe the non-blocking character of real electrodes. The model of Chang-Jaffe [18], proposed long ago, reminds the model to describe the surface evaporation in diffusion problems [32]. The ohmic model assumes that the electric current across the electrode is proportional to the surface electric field [33], whereas the diffusive model [25] that the current is proportional to the surface gradient of ionic concentrations. All models are phenomenological. This means that they describe the electrode non-blocking properties by means of macroscopic parameters, that depends on the physical properties of the solution and of the electrode in contact with it. This description is an over simplification of the real problem. A more rigorous analysis has to be done starting from a microscopical point of view. However, as all phenomenological theories, the models discussed above to describe real electrodes allow a description of the electrode-phenomena based on a small number of parameters, and could be useful for practical applications. Of course, the phenomenological parameters introduced in the models depend on the physical properties of the electrode and of the solution in contact with.

In fact, the boundary conditions for the ions concentrations have the form of four equations, two at the electrode at $z = -L/2$ and two at the electrode at $z = L/2$, describing the electrodes processes for the positive and negative ions. They are based on the assumption that the processes of charge transfer between the molecules of impurities generating the ions, or ions in the solution are limited by energy barriers which determine the activation energy, φ, of the corresponding electrochemical reactions [34]. In consequence, they determine the rates of generation and neutralization of the ions. For instance, the rate of neutralization of a negative ion occurring by the transfer of an electron from the ion to the electrode is equal to

$$K_r = k_r\, e^{-\varphi/K_B T}, \tag{7}$$

where k_r is a constant. A similar formula can be used for the generation constant of positive ions occurring by the transfer of an electron from a neutral molecule to the electrode. Absolute values of the parameters φ and k_r are not essential, only the resulting K_r value is important. The blocking case is recovered by assuming $K_r = 0$. The energy barrier is changed by the presence of the external electric filed $E(z, t)$ existing at the electrode. It is increased or decreased by

$$\Delta\varphi(\pm L/2, t) = |E(\pm L/2, t)| q\ell, \tag{8}$$

where ℓ is the thickness of the sub-electrode region, of the order of several molecular lengths. As a result of the above assumption, the conservation of ions at the electrode takes the form

$$j_p = N_p K_r e^{-\Delta\varphi/K_B T} - N_0 K_r e^{\Delta\varphi/K_B T}, \tag{9}$$

$$j_m = N_m K_r e^{\Delta\varphi/K_B T} - N_0 K_r e^{-\Delta\varphi/K_B T}, \tag{10}$$

for the positive and negative ions, respectively, at the electrode at $z = L/2$. In equations (9) and (10) the first term on the right-hand sides denote the numbers of ions which are neutralized, and the second term the number of ions generated at the electrodes in course of accepting or donating the electrons to the neutral molecules. They have the same form of Butler-Volmer equation for the current across the electrode, where $\Delta\varphi$ is proportional to the over potential [26].

In the framework of small applied potential, such that the drop of potential in the sub-electrode region is small with respect to $K_{\rm B}T/q$, where the Poisson–Nernst–Planck model works, from equations (9) and (10) we get, expanding the exponential function to the first order in $\Delta\varphi/K_{\rm B}T$,

$$j_p = K_r\left\{(N_p - N_0) + 2N_0\frac{q}{K_{\rm B}T}\ell E\right\} \tag{11}$$

$$j_m = K_r\left\{(N_m - N_0) - 2N_0\frac{q}{K_{\rm B}T}\ell E\right\}. \tag{12}$$

Note that in equations (11) and (12) the first term is proportional to the ionic concentration variation with respect to the value of equilibrium, as in the model of Chang-Jaffe, according to which

$$j_a(L/2,t) \propto [N_a(L/2,t) - N_0], \tag{13}$$

whereas the second one is proportional to the surface electric field, as in the ohmic model, where

$$j_a(L/2,t) \propto E(L/2,t). \tag{14}$$

The importance of one term with respect to the other one depends on the thickness of the sub-electrode region. As it follows from equations (11) and (12) the phenomenological parameter appearing in the model of Chang-Jaffe coincides with K_r, and it depends by the activation energy of the corresponding chemical reaction of the ions on the electrode. Similar conclusion is valid for the phenomenological parameter entering the ohmic model.

In a recent past, the exchange current has been modeled with the first or with the second terms. In the present paper we discuss the non-equivalence between the Chang-Jaffe, ohmic, and diffusive models.

In our analysis we assume that the electrodes are identical. In this framework, in the absence of an external power supply, the difference of potential between the two electrodes is identically zero. In the absence of selective ionic adsorption, i.e. same chemical potential for the positive and negative ions with respect to the limiting electrodes, the electric potential is constant in the cell. In the presence of an external power supply, an electric field exists in the cell. Assuming that the electrodes are connected to the power supply in such a manner that $V(\pm d/2,t) = \pm(V_0/2)\exp(i\omega t)$, from the assumption that the electrodes are identical, the potential across the sample is such that $V(-z,\,t) = -V(z,\,t)$. Similar considerations hold true for the ionic densities. From this consideration it follows that, in our framework, all the functions involved in the description, i.e. ionic bulk densities and electric potential, are odd functions of z. For this reason the number of integration constants is just three. This can be easily understood, without any calculation, in the following manner. If the electrodes are identical in all aspects with respect to the ions, on one electrode positive charges are leaving the sample, when the electrode is positive, and on the other the same number of positive charges is entering in it, since the corresponding electrode is negative. The same discussion holds for negative charges. Consequently the number of positive and negative charges remains constant in the cell. This implies that, with our cartesian reference frame, the bulk densities of ions are odd functions of z-coordinate.

III.B.1. Ohmic electrodes. In the case the electrodes are ohmic, the current density of particles at the electrodes is proportional to the local electric field $j_a = (\gamma_a/\pm q)E(\pm L/2)$, where γ_p and γ_n are the surface conductivity for cations and anions respectively.

For what concerns the ionic current densities, in the framework of the ohmic model [33], the proposed boundary conditions, at $z = \pm L/2$, are [35]

$$\frac{\partial u_p}{\partial z} + (1-\kappa_p)\frac{\partial u_v}{\partial z} = 0, \tag{15}$$

$$\frac{\partial u_n}{\partial z} - (1-\kappa_n)\frac{\partial u_v}{\partial z} = 0, \tag{16}$$

where $\kappa_a = \gamma_a/\sigma_a$ is the reduced surface conductivity and $\sigma_a = qN_0D_a/V_{\rm th}$ is the bulk conductivity of the ions at thermodynamic equilibrium.

III.B.2. Chang-Jaffe electrodes. According to the Chang-Jaffe [18] model the particles current at the electrodes is proportional to the ionic bulk density variation from concentration at thermodynamic equilibrium and it can be written as $j_a = H_a(N_a - N_0)$, where H_a are the reaction rates. The corresponding BCs at the electrodes are

$$\frac{\partial u_p}{\partial z} + \frac{\partial u_v}{\partial z} + h_p u_p = 0, \tag{17}$$

$$\frac{\partial u_n}{\partial z} - \frac{\partial u_v}{\partial z} + h_n u_n = 0, \tag{18}$$

where $h_a = H_a/D_a$ are the CJ parameters.

III.B.3. Diffusion type BCs. Introducing now the diffusion model [25], the particles current of the ions, a, at the electrodes is $j_a(\pm L/2) = \zeta_a\nabla N_a$, where ζ_a are diffusion constants at the interface, then the ionic current densities at $z = \pm L/2$ give the diffusion model BCs

$$(1+\chi_p)\frac{\partial u_p}{\partial z} + \frac{\partial u_v}{\partial z} = 0, \tag{19}$$

$$(1+\chi_n)\frac{\partial u_n}{\partial z} - \frac{\partial u_v}{\partial z} = 0, \tag{20}$$

where $\chi_a = \zeta_a/D_a$ are reduced diffusion constants.

IV. equivalence

IV.A. OBCs and CJBCs equivalence

In the following we calculate the integration constants using the BCs. By substituting equations (3)–(5) into equations (15) and (16) and in equations (17) and (18) we get for $\kappa_a \neq 1$

$$\left(\frac{\nu_1}{1-\kappa_p}-\frac{1-k_1}{2\nu_1 L_{\mathrm{D}}^2}\right)C_1\cosh\beta_1+\left(\frac{\nu_2}{1-\kappa_p}-\frac{1-k_2}{2\nu_2 L_{\mathrm{D}}^2}\right)C_2\cosh\beta_2+A=0, \tag{21}$$

$$\left(\frac{k_1\nu_1}{1-\kappa_n}+\frac{1-k_1}{2\nu_1 L_{\mathrm{D}}^2}\right)C_1\cosh\beta_1+\left(\frac{k_2\nu_2}{1-\kappa_n}+\frac{1-k_2}{2\nu_2 L_{\mathrm{D}}^2}\right)C_2\cosh\beta_2-A=0, \tag{22}$$

and

$$\left(\nu_1-\frac{1-k_1}{2\nu_1 L_{\mathrm{D}}^2}+h_p\tanh\beta_1\right)C_1\cosh\beta_1+\left(\nu_2-\frac{1-k_2}{2\nu_2 L_{\mathrm{D}}^2}+h_p\tanh\beta_2\right)C_2\cosh\beta_2+A=0, \tag{23}$$

$$\left(k_1\nu_1+\frac{1-k_1}{2\nu_1 L_{\mathrm{D}}^2}+h_n k_1\tanh\beta_1\right)C_1\cosh\beta_1+\left(k_2\nu_2+\frac{1-k_2}{2\nu_2 L_{\mathrm{D}}^2}+h_n k_2\tanh\beta_2\right)C_2\cosh\beta_2-A=0, \tag{24}$$

respectively, where $\beta_1=\nu_1 L/2$, and $\beta_2=\nu_2 L/2$.

The two models are equivalent if they predict the same u_p, u_n and u_v, i.e. if the systems determining C_1, C_2 and A are the same for the two models. This implies that, comparing equations (21) and (22) with equations (23) and (24) respectively, the phenomenological parameters of the two models should be such that

$$h_a=\frac{\kappa_a}{1-\kappa_a}\nu_1\coth\beta_1,\quad\text{and}\quad h_a=\frac{\kappa_a}{1-\kappa_a}\nu_2\coth\beta_2. \tag{25}$$

Except for the trivial solution, equation (25) cannot be satisfied for $\nu_1\neq\nu_2$. It follows that in the general case the ohmic model is not equivalent to the Chang-Jaffe model. Nevertheless, the two models are equivalent in two particular cases:

(i) When $D_p=D_n$, and the two electrodes are identical, that implies $\kappa_p=\kappa_n=\kappa$ or $h_p=h_n=h$, a simple calculation shows that $k_1=-1$, $k_2=1$, $C_2=0$. It follows that u_p, u_n and u_v, are given by

$$u_p(z)=C\,\sinh(\nu_1 z), \tag{26}$$

$$u_n(z)=-C\,\sinh(\nu_1 z), \tag{27}$$

$$u_v(z)=-\frac{C}{2L_{\mathrm{D}}^2\nu_1^2}\,\sinh(\nu_1 z)+Az, \tag{28}$$

in agreement with [4]. In this case a relation exists between the phenomenological parameters of the two models given by equation (25) that rewrite as

$$h=\frac{\kappa}{1-\kappa}\nu_1\coth\beta_1. \tag{29}$$

Note that to a real parameter of the OBC corresponds a complex parameter of the CJBC. Note that a similar result was found in [24], concerning the equivalence between the CJBC and a Langmuir type adsorption-desorption process at the electrodes when both types of ions have the same mobility.

(ii) In the case where only the ions of a given sign are mobile, for instance $D_n=0$ and hence $u_n=0$, each model is described by one parameter at the electrodes. Therefore one finds that the relation between h_p and κ_p is given by the left part of equation (25). In this case u_p and u_v, are given by

$$u_p(z)=C\,\sinh(\nu_1 z), \tag{30}$$

$$u_v(z)=-\frac{C}{2\Lambda^2\nu_1^2}\,\sinh(\nu_1 z)+Az, \tag{31}$$

where $\Lambda=\sqrt{\varepsilon_s k_{\mathrm{B}}T/(N_0 q^2)}$ is the length of Debye for the present case. In this particular case, equivalence between the two models has been discussed in [20, 21].

IV.A.1. Approximated equivalence. As it was shown in the previous paragraph, there is no analytical equivalence between the CJBCs and the OBCs for the general case where (i) both anions and cations are mobile, and (ii) they have different diffusion constants. Nevertheless, one can construct an analytical but approximate equivalence by (i) introducing a concentration length ℓ_c that gives the distance from the electrode over which an appreciable concentration gradient is present, and (ii) assuming that the gradient profile is linear. Then the surface current densities according to the CJBCs may be rewritten as

$$j_a=H_a(N_a-N_0)=(H_a\,\ell_c)\nabla N_a. \tag{32}$$

Using the latter result in equations (17) and (18) and comparing with equations (15) and (16) that describe the OBCs, one finds

$$h_a=\frac{\kappa_a}{1-\kappa_a}\,\ell_c^{-1} \tag{33}$$

that in terms of H_a becomes $H_a=h_a\,D_a$. Note that we assumed a linear profile of the concentration gradient that is not probably a good approximation for large concentration gradients, where the validity of Fick's law itself is questionable. The concentration gradient length ℓ_c is expected to be of the order of Debye's length for ions that have about the same mobility. For appreciable different mobilities one expects that it will depend on the ion type.

IV.B. OBCs and DBCs equivalence

Inspection of the equations (15) and (16) expressing the OBCs and of equations (19) and (20) for the DBCs shows that the two types of BCs are equivalent if

$$(1+\chi_p)(1-\kappa_p)=1, \tag{34}$$

$$(1+\chi_n)(1-\kappa_n)=1, \tag{35}$$

Table 1. Comparisons of LEVMW CNLS fit results, using various fitting models and boundary conditions with modulus weighting, for various admittance-level exact PNP data sets with full charge dissociation.

Data model OBPNP κ_n	Fit model	S_F PDRMS	$C_\infty[F] \times 10^{10}$	$R_\infty[\Omega] \times 10^{-6}$	N_0 [cm^{-3}] $\times 10^{-14}$	Π_m	D_n [cm^2 s^{-1}] $\times 10^7$	ρ_p ρ_n	H_p [cm s^{-1}] H_n [cm s^{-1}]
0	PNP	8.8×10^{-7}	1.187	2.162	4.004	10.000	8.200	—	—
		3.3×10^{-6}						—	—
10^{-8}	CJPNP	1.4×10^{-6}	1.186	2.165	3.997	10.000	8.200	—	—
		5.2×10^{-6}						4.879×10^{-6}	8.001×10^{-10}
10^{-7}	CJPNP	1.3×10^{-6}	1.186	2.165	3.997	10.000	8.200	1.229×10^{-4}	2.015×10^{-8}
		1.5×10^{-3}						3.650×10^{-5}	5.986×10^{-9}
10^{-6}	CJPNP	1.6×10^{-6}	1.186	2.165	3.997	10.000	8.200	1.414×10^{-3}	2.318×10^{-7}
		2.4×10^{-4}						3.467×10^{-4}	5.685×10^{-8}
10^{-5}	CJPNP	2.8×10^{-4}	1.186	2.165	3.995	9.910	8.197	1.402×10^{-2}	2.299×10^{-6}
		0.034						3.479×10^{-3}	5.704×10^{-7}
10^{-4}	CJPNP	2.4×10^{-4}	1.186	2.165	3.997	9.980	8.193	1.843×10^{-1}	3.020×10^{-5}
		0.021						3.258×10^{-2}	5.339×10^{-6}

Note: OBPNP designates the PNP model with ohmic boundary conditions, and CJPNP denotes that model with Chang-Jaffe boundary conditions. In the first row and column κ_n is the principal dimensionless ohmic boundary condition parameter for positive charges. The corresponding one for positive charges is $\kappa_p = \kappa_n/2$. When these parameters are zero, there is full blocking at the electrodes of mobile charges. SR stands for a data range beginning at about 0.1 Hz, while for all other rows the lowest data point was calculated for a frequency value of about 1.6×10^{-5} Hz. The D_n and $M = L/2L_D$ parameter values were calculated from the four free parameters listed in the table but since M estimates were 465 for all conditions, they are not included in the table. In the fits, the free reaction-rate parameters $\rho_p = (L/2D_p)\kappa_p$, $\rho_n = (L/2D_n)\kappa_n$ are dimensionless and their values are shown in column 9. They are transformed to the $H_a = 2D_a\rho_a/L$, where $a = p, n$, parameters of the tenth column and have dimensions of cm s^{-1}. $\Pi_m = D_n/D_p$, $C_\infty = \varepsilon_s A/L$, $R_\infty = (q^2/KT)N_0(D_p + D_n)L/A$.

or equivalently

$$\chi_p = \frac{\kappa_p}{1 - \kappa_p}, \tag{36}$$

$$\chi_n = \frac{\kappa_n}{1 - \kappa_n}. \tag{37}$$

Therefore, the two models are equivalent. Note that the case $\kappa_a \leqslant 1$ implies $\zeta_a \leqslant 0$.

Of course all models reduce to the case of perfectly blocked electrodes when $\kappa_a = h_a = \zeta_a = 0$.

V. Numerical analysis

In the previous section, we analytically showed that the PNP model with ohmic boundary conditions (OBPNP) and with Chang-Jaffe boundary conditions (CJPNP) are not equivalent in general. In the present section we aim to test how this non-equivalence appears on the admittance/impedance level by comparing the models numerically. In order to carry out numerical comparisons between the OBPNP and CJPNP models, we use data sets calculated from the OBPNP model and we fit them with the CJPNP model. Fitting was carried out using the LEVMW[4] impedance spectroscopy computer program at one or more of the four immittance levels, all using modulus weighting. We assume $D_n = 8.2 \times 10^{-7}$ cm^{2}s^{-1}, $D_p = 10 \times D_n$, $N_0 = 4 \times 10^{14}$ cm^{-3}, $\varepsilon_s = 6.7 \times \varepsilon_0$. The geometrical parameters of the sample are $L = 1$ μm and $A = 2$ cm^2. The temperature is fixed to $T = 290$ K. In addition to the the model parameters fit estimates listed in table 1, graphs are included showing the admittance frequency response (in Ω^{-1}) for some of the fits of the six rows in the table. These graphs were produced directly from the LEVMW fits. They are appropriate for situations, such as most of the six fits here, where the fits are so close that ordinary log–log frequency response plots show no observable difference between data points (red) and fit lines (blue). They clarify such ambiguity by including both direct-fit residual plots and relative residual ones, with real-part results in red and imaginary part ones in blue. The relative residual results are useful here in showing any important low-frequency fit discrepancies.

The results of rows 1–6 of the table and figures 1–4 compare CJPNP model fit results with exact OBPNP data sets varying from full blocking (reduced surface conductivity: $\kappa_n = 0$) to appreciable reactions of the mobile ions at the electrodes, as in row 6. Incidentally the fully blocking results of row 1 are essentially the same both for the frequency range starting at 0.1 Hz and for the one starting at 10^{-5} Hz, not surprising since here both the data and the model involve just PNP response. Note that the fit parameter estimates of columns 4–8 of the table are close to the input values used in calculating the OBPNP data sets.

As the results of rows 1–6 of the table show, the partially blocking fits of rows 2 and 3 are still good, but while only one reaction rate parameter could be estimated from the row 2 data set, the expected two rate parameter values were obtained for rows 3 and 4, with their uncertainties appreciably larger for the row 6 results than for the row 3 ones.

Finally we compare the two models by using the above results and equation (25) that relates the OBCs parameters with those of the CJBCs model. Figure 5 shows (a) H_n versus κ_n,

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[4] The Windows version, LEVMW, of the comprehensive LEVM fitting and inversion program can be downloaded at no cost by accessing http://jrossmacdonald.com. It includes an extensive manual, executable and full source code, and many fitting models, including the HN and CJPNP ones.

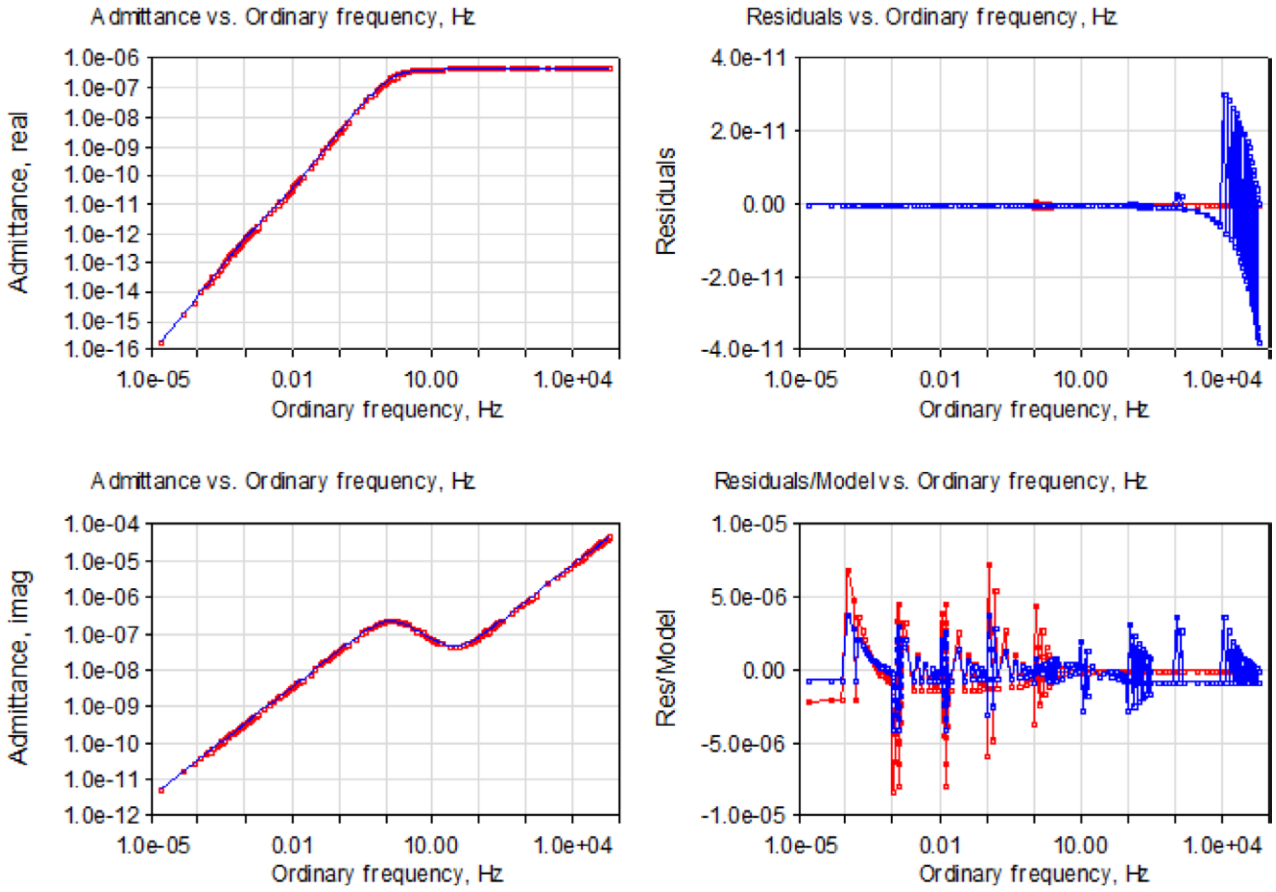

Figure 1. Admittance-level fit results of exact completely blocking PNP data with the completely blocking PNP model. Estimated values of the four free fit parameters of the model are shown in row 1 of table 1. Admittance in Ω^{-1}.

and (b) H_p versus κ_p. The continuous line is calculated from equation (25) while the filled points are the fitting results given in table 1. In both cases we took ℓ_c equal to Debye's length. This approximation seems reasonable for the fast anions (see figure 5(a)) but it proves poor for the slow cations (see figure 5(b)). Certainly one expects that ℓ_c, even in the framework of a model based on the validity of Fick's law for the diffusion phenomenon, depends on the diffusion constant and on the surface conductivity and/or the surface reaction rate. Therefore ℓ_c is expected to depend on the type of ions and eventually to vary with the surface conductivity and/or the reaction rate. In figure 5(b), the dashed line is a fit with ℓ_c as a free parameter. The best fit is obtained for $\ell_c = 0.019\,L_{\mathrm{D}}$. One can obtain fits of the same quality using as a free parameter either the surface conductivity or supposing a fractional dependence of ℓ_c on Debye's length (not shown), related to an anomalous diffusion in the surface layer [20], or eventually to a surface diffusion constant that is different from the bulk one. It is evident from the above discussion, that one cannot obtain the correct values of the OBCs model parameters fitting the impedance with CJBCs and therefore the models are definitely not equivalent in what concerns their surface parameters. The deviation between the two models increases with increasing electrode conductivity in accordance with equation (25). This conclusion also shows that good fit quality does not always result to the correct values of the underlined physical parameters. Nonetheless, note that the fittings give the correct values for the bulk parameters.

Since both the OBCs and the CJBCs are plausible, but are not always equivalent, particularly for situations with different mobilities of the positive and negative charges and large reaction rates, as shown in the last row of the table, it is uncertain which one or neither would be most appropriate for analyzing actual experimental data sets. It is thus important to carry out OBPNP and CJPNP model fitting of real data of the above type to resolve this issue and discover which boundary conditions are the more physically appropriate for typical impedance spectroscopy data.

VI. Conclusion

We have investigated the problem of equivalence between the ohmic, the diffusion and the Chang and Jaffe BCs in the framework of the PNP model for the general case where anions and cations are both mobile and they may have different mobility. We have shown that the ohmic and diffusion type electrode models are formally equivalent, while the analytical equivalence between the Chang and Jaffe and the ohmic types is restricted in two particular cases where either all ions have the same bulk mobility or only the ion of a given sign are mobile and the sample is limited by identical electrodes. The latter case was alredy studied in [20, 21]. When the symmetry of the

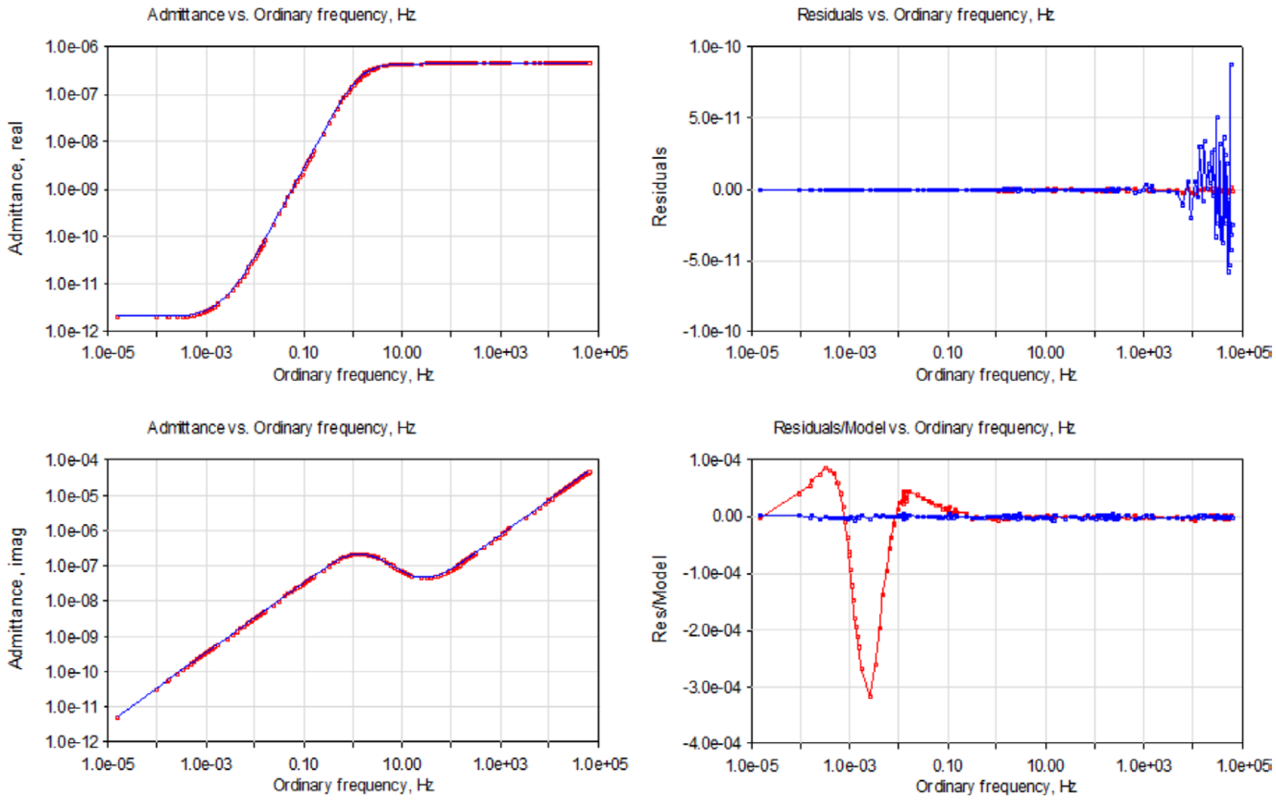

Figure 2. Admittance-level fit results of exact partly blocking PNP data with the partially blocking CJPNP model for $\kappa_n = 10^{-8}$. Estimated values of the five free fit parameters of the model are shown in row 2 of table 1. Admittance in Ω^{-1}.

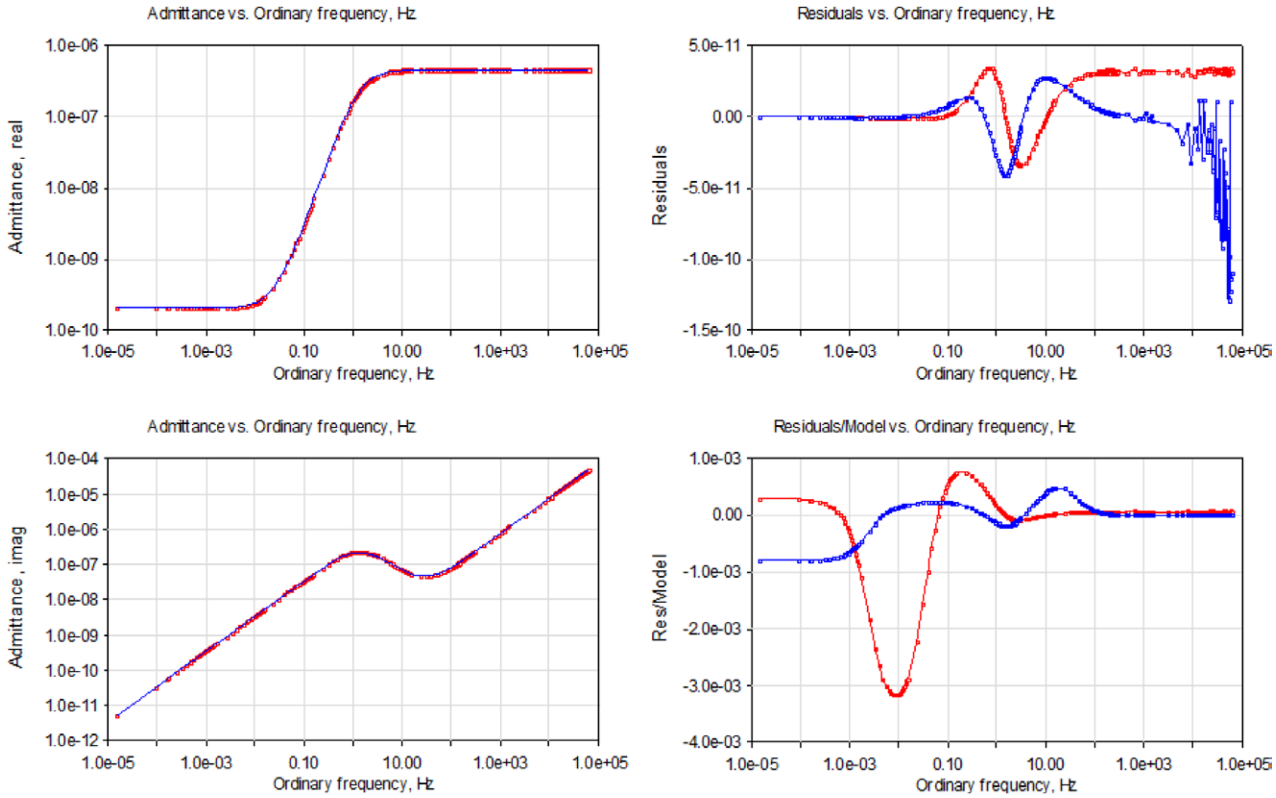

Figure 3. Admittance-level fit results of exact partly blocking PNP data with the partially blocking CJPNP model for $\kappa_n = 10^{-6}$. Estimated values of the five free fit parameters of the model are shown in row 4 of table 1. Admittance in Ω^{-1}.

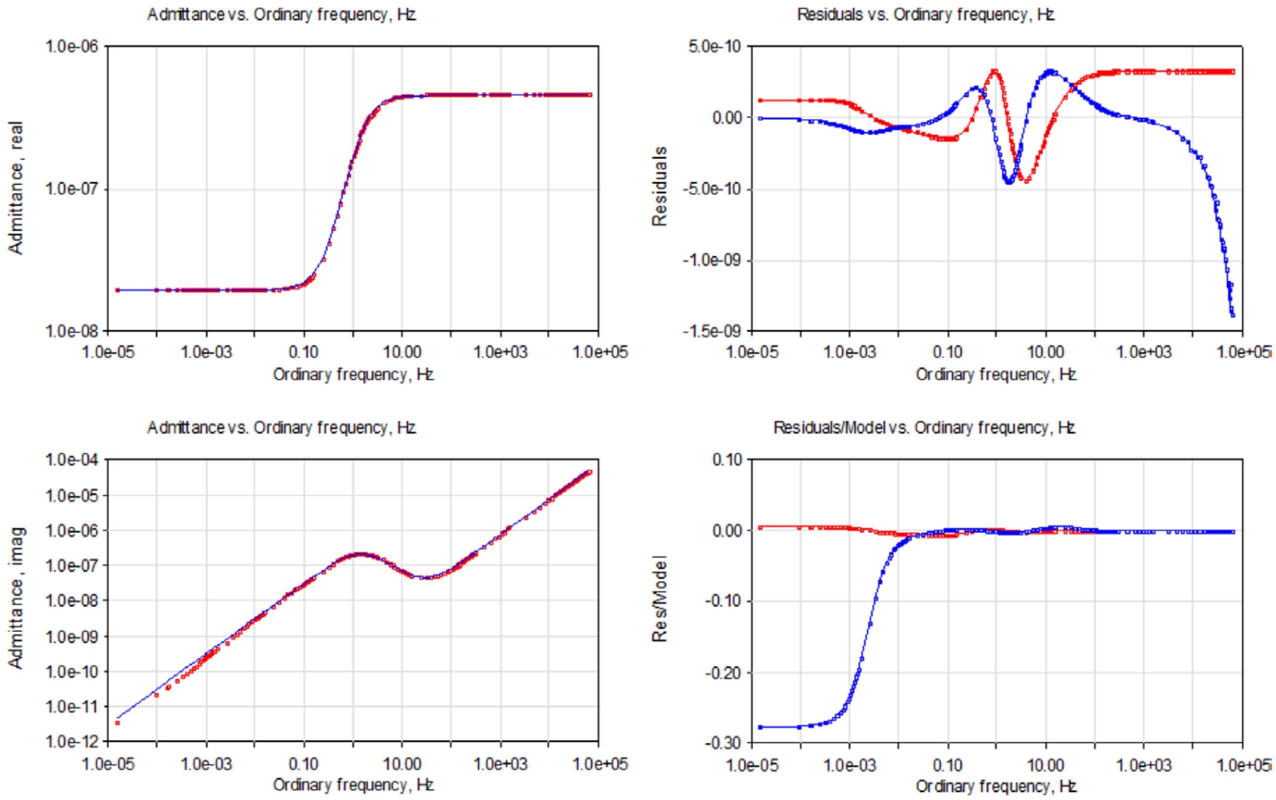

Figure 4. Admittance-level fit results of exact partly blocking PNP data with the partially blocking CJPNP model for $\kappa_n = 10^{-4}$. Estimated values of the six free fit parameters of the model are shown in row 6 of table 1. Admittance in Ω^{-1}.

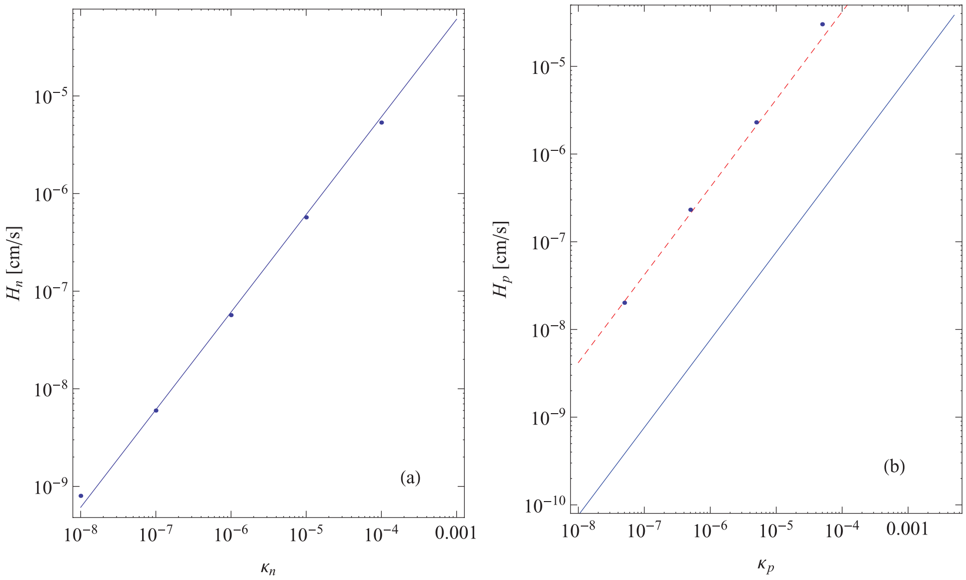

Figure 5. H_a versus κ_a, where $a = p, n$. Solid points are calculated from fitting the OBCPNP model with the CJBCPNP model, given at table 1. (a) H_n versus κ_n. Blue continuous line is calculated from equation (25) taking ℓ_c equal to Debye's length. The agreement is reasonable for the fast anions. (b) H_p versus κ_p. Blue continuous line is calculated from equation (25) taking ℓ_c equal to Debye's length. In the case of the slow cations there is a large deviation between the two models, that increases with increasing surface conductivity. Red dashed line has been calculated with $\ell_c = 0.019\,L_{\mathrm{D}}$.

sample is broken because the mobilities of the positive and negative charges are different and both are non-zero, the two models are not equivalent from the analytical point of view. Nonetheless, fitting the same data-set with the two models may result in fittings of the same quality, for low enough electrode conductivity, but the obtained fit parameters characterizing the electrodes are different. The numerical fitting results of rows 2–6 of table 1 further demonstrate the increasing non-equivalence, of the two models, as the electrode reaction-rate parameters increase in size. In all cases both models give the same bulk parameters.

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Appendix A

The characteristics complex lengths $\nu_{1,2}^{-1}$, $\ell_{p,n}$ and constants $k_{1,2}$ appearing into equations (3)–(5) are defined by

$$\nu_{1,2} = \frac{1}{\sqrt{2}\,L_{\rm D}} \sqrt{1 + {\rm i}\omega L_{\rm D}^2 \frac{D_p + D_n}{D_p D_n} \pm \sqrt{1 + \left({\rm i}\omega L_{\rm D}^2 \frac{D_n - D_p}{D_n D_p}\right)^2}}. \tag{A.1}$$

$$\begin{aligned} \frac{1}{\ell_p^2} &= \frac{1}{2L_{\rm D}^2}\left(1 + 2{\rm i}\omega\,\frac{L_{\rm D}^2}{D_p}\right) \\ \frac{1}{\ell_n^2} &= \frac{1}{2L_{\rm D}^2}\left(1 + 2{\rm i}\omega\,\frac{L_{\rm D}^2}{D_n}\right), \end{aligned} \tag{A.2}$$

and

$$k_{1,2} = -2L_{\rm D}^2\left(\nu_{1,2}^2 - \frac{1}{\ell_p^2}\right), \tag{A.3}$$

as discussed in [30, 31]. In the static case, where $\omega = 0$,

$$\nu_1 = \frac{1}{L_{\rm D}}, \qquad \nu_2 = 0, \tag{A.4}$$

$$\frac{1}{\ell_p^2} = \frac{1}{\ell_n^2} = \frac{1}{2L_{\rm D}^2}, \tag{A.5}$$

$$k_1 = -1, \quad \text{and} \quad k_2 = 1. \tag{A.6}$$

We stress that in this case, as discussed below, also a linear contribution to $u_p(z)$ and $u_n(z)$, not present in equations (4) and (5), is possible.

In the case where $D_p = D_n = D$, we get

$$\nu_1 = \frac{1}{L_{\rm D}}\sqrt{1 + {\rm i}\omega\frac{L_{\rm D}^2}{D}}, \qquad \nu_2 = \sqrt{{\rm i}\frac{\omega}{D}}, \tag{A.7}$$

$$\frac{1}{\ell_p^2} = \frac{1}{\ell_n^2} = \frac{1}{2L_{\rm D}^2}\left(1 + 2{\rm i}\omega\frac{L_{\rm D}^2}{D}\right), \tag{A.8}$$

$$k_1 = -1, \quad \text{and} \quad k_2 = 1. \tag{A.9}$$

Appendix B

In the static case, u_p, u_n and u_v are solutions of the ordinary differential equations

$$\frac{\rm d}{{\rm d}z}(u_p' + u_v') = 0, \tag{B.1}$$

$$\frac{\rm d}{{\rm d}z}(u_n' - u_v') = 0, \tag{B.2}$$

and

$$u_v'' = -\frac{1}{2L_{\rm D}^2}(u_p - u_n), \tag{B.3}$$

where the prime means derivation with respect to z, $f' = {\rm d}f/{\rm d}z$. The relevant boundary conditions for the ionic current densities are

$$u_p' + u_v' = \kappa_p u_v', \tag{B.4}$$

$$u_n' - u_v' = -\kappa_n u_v', \tag{B.5}$$

for the ohmic model, and

$$u_p' + u_v' = -h_p u_p, \tag{B.6}$$

$$u_n' - u_v' = -h_n u_n, \tag{B.7}$$

for the Chang-Jaffe model, at $z = \pm L/2$, and

$$u_v(\pm L/2) = \pm u_0/2, \tag{B.8}$$

for the electric potential.

The solutions we are looking for are

$$u_p = C_1 \sinh(z/L_{\rm D}) + C_2 z, \tag{B.9}$$

$$u_n = -C_1 \sinh(z/L_{\rm D}) + C_2 z, \tag{B.10}$$

$$u_v = -C_1 \sinh(z/L_{\rm D}) + Az, \tag{B.11}$$

that are the limit of the general formulae (3)–(5) for $\omega \to 0$. By substituting equations(B.9)–(B.11) into equations (B.4), (B.5) and (B.8) and equations (B.6) and (B.7) we get

$$\frac{1}{L_{\rm D}}\frac{\kappa_p}{1 - \kappa_p}\cosh M\, C_1 + \frac{1}{1 - \kappa_p}C_2 + A = 0, \tag{B.12}$$

$$\frac{1}{L_{\rm D}}\frac{\kappa_n}{1 - \kappa_n}\cosh M\, C_1 - \frac{1}{1 - \kappa_n}C_2 + A = 0, \tag{B.13}$$

for the ohmic model, and

$$h_p \sinh M\, C_1 + (1 + h_p d/2)\, C_2 + A = 0, \tag{B.14}$$

$$h_n \sinh M\, C_1 - (1 + h_n d/2)\, C_2 + A = 0, \tag{B.15}$$

for the Chang-Jaffe model, where $M = L/(2L_{\rm D})$, is usually very large with respect to 1. The two models are equivalent if

$$\frac{1}{L_{\rm D}}\frac{\kappa_p}{1 - \kappa_p}\cosh M = h_p \sinh M, \tag{B.16}$$

$$\frac{1}{1-\kappa_p} = 1 + h_p \frac{L}{2}, \tag{B.17}$$

and a similar system of equations for κ_n and h_n, that imply $\tanh M = M$. Since this condition is not verified for large M the two models are not equivalent, in the sense that it is impossible to choose a value of H_p by means of which the Chang-Jaffe boundary conditions are identical to the ohmic boundary conditions. From this result we infer that even in the static case the ohmic and Chang-Jaffe model are not equivalent. The equivalence exists, as discussed in [21, 23], in the case where only one group of ions is mobile.

Note that in the symmetric case, where $\kappa_p = \kappa_n = \kappa$, and $h_p = h_n = h$, a simple calculation shows that $C_2 = 0$. In this situation equations (B.12) and (B.13) and equations (B.16) and (B.17) reduce to

$$\frac{1}{L_{\mathrm{D}}} \frac{\kappa}{1-\kappa} \cosh M \; C_1 + A = 0, \tag{B.18}$$

$$h \sinh M \; C_1 + A = 0, \tag{B.19}$$

from which it follows that the two model are equivalent if

$$h = \frac{\kappa}{L_{\mathrm{D}}(1-\kappa)} \coth M, \tag{B.20}$$

that coincides with equation (29) written for the case under consideration.

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