

Reply to “Comment on ‘Modeling of electrode polarization for electrolytic cells with a limited ionic adsorption’”

Atsushi Sawada

Performance Materials Advanced Technologies, Merck Ltd., Aikawa, Kanagawa 243-0303, Japan

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The dielectric properties of dilute electrolytic solution cells have been measured in a low-frequency region, and the dielectric spectra have been analyzed in terms of space-charge polarization by using the Nernst-Planck (NP) model in the presence of ionic adsorption on electrodes [Phys. Rev. E **88**, 032406 (2013)]. In the NP model, the internal electric field of the cell is considered to be approximately equal to the external field. In a Comment by Alexe-Ionescu *et al.* [Phys. Rev. E **89**, 056401 (2014).] on our paper [Phys. Rev. E **88**, 032406 (2013)], they claim the invalidity of the NP model and the necessity of the conventional Poisson-Nernst-Planck (PNP) model for the data analysis. Their criticisms are, however, originated from a viewpoint for determining the internal electric field, that is different from our approach. In this Reply, we show the validity of the NP model referring to our previous paper in which the conventional PNP model has been modified so as to correctly describe the actual internal field.

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The frequency dependences of the complex dielectric constant of dilute electrolytic solution cells have recently been analyzed in terms of space-charge polarization by using the Nernst-Planck (NP) model in the presence of ionic adsorption on electrodes [1]. The dilute electrolytic solutions were prepared using chlorobenzene doped with tetrabutylammonium tetrphenylborate (TBATPB) at different concentrations. The data analysis has been carried out assuming that the cell has blocking electrodes. In the NP model, the internal electric field of the cell is considered to be approximately equal to the external field. In Ref. [2], Alexe-Ionescu *et al.* have criticized the work of Ref. [1] at some points in the analytical process. However, most of the criticisms are originated from a viewpoint for determining the internal electric field, that is different from our approach.

If an external voltage is applied to the cell, TBA⁺ and TPB⁻ ions drift to the electrodes. Since the movements of the ions are blocked at the electrodes, the internal electric field becomes inhomogeneous due to the redistributed ions. Therefore, the internal field has to be determined satisfying Poisson's equation, and the analysis of the complex dielectric constant should be performed by using the Poisson-Nernst-Planck (PNP) model. The main criticism in Ref. [2] is just this point. On the other hand, we have shown, in the previous paper [3], that although the internal field of the dilute electrolytic cell cannot be determined correctly by the conventional PNP model, it can be performed by a pragmatic PNP model in which the contribution of the space-charge polarization is included in the dielectric constant of Poisson's equation. [We designate the Poisson-Nernst-Planck-Sawada (PNPS) model for the pragmatic PNP model here and throughout.] Moreover, further analysis [4,5] has revealed an important fact that, although the frequency-dependent curve of the complex dielectric constant due to the space-charge polarization calculated using the PNPS model is totally different from that using the PNP model, it becomes very close to that using the NP model. In Ref. [5], numerical calculation was carried out for obtaining the complex dielectric constants at different frequencies because it was difficult to solve the PNPS equations analytically. Since we

would focus on the adsorption-desorption phenomena of the ions on the electrodes and the capacity at the interface between the electrode and the electrolytic solution as a main discussion point, we have employed the NP model rather than the PNPS model in Ref. [1] for analyzing the space-charge polarization to prevent the complexity of the calculation process of the PNPS model. In this sense, the criticisms in Ref. [2] are strongly related to our previous papers [3–5] rather than the work of Ref. [1]. The difference between the PNPS and the PNP models is as follows.

Let us consider an experimental system for the impedance measurement of a dielectric material containing monovalent positive and negative mobile charges, which is embedded between parallel-plate blocking electrodes. We assume that the recombination of the positive and negative mobile charges can be neglected, and the number density (number per unit volume) of the positive mobile charges n_{p0} is equal to that of the negative mobile charges n_{n0} and $n_{p0} = n_{n0} = c_0$. We also assume that both mobile charges are distributed uniformly in the dielectric material in the absence of an external electric field. We restrict our consideration to a one-dimensional case with the transport of mobile charges in the x direction under an electric field applied externally.

In the PNPS model, the internal electric field $E(x,t)$ is expressed as

$$\partial E(x,t)/\partial x = q[n_p(x,t) - n_n(x,t)]/[\varepsilon_0\varepsilon_r(t)], \quad (1)$$

using Poisson's equation assuming that the number density of positive mobile charges is $n_p(x,t)$ and that of negative mobile charges is $n_n(x,t)$ in space and time. In Eq. (1), q is the elementary charge, ε_0 is the dielectric constant in vacuum, and $\varepsilon_r(t)$ is the relative dielectric constant of the dielectric material. Here, $\varepsilon_r(t)$ includes the contribution of the space-charge polarization and varies with time. Providing the relaxation function $\Phi(t)$ that takes monotonically increasing values between 0 and 1 with time, $\varepsilon_r(t)$ is written as [3]

$$\varepsilon_r(t) = \varepsilon_s + \varepsilon_{r0}\Phi(t), \quad (2)$$

where ε_s is the relative dielectric constant of the dielectric (matrix) material and ε_{r0} is the maximum value of the relative dielectric constant due to the space-charge polarization. Here, ε_s consists of the contribution of electronic, atomic, and dipole polarizations and has a time-dependent property; nevertheless, the value of ε_s is considered to be constant in the time domain in the present study. In the PNP model, the dielectric constant is considered to be $\varepsilon_r(t) = \varepsilon_s$.

The integration of Eq. (1) gives the intensity of the electric field,

$$E(x,t) = E(0) + \frac{q}{\varepsilon_0 \varepsilon_r(t)} [f_p(x,t) - f_n(x,t)], \quad (3)$$

where

$$f_p(x,t) = \int_0^x n_p(x,t) dx, \quad (4)$$

$$f_n(x,t) = \int_0^x n_n(x,t) dx, \quad (5)$$

and $E(0)$ is the electric field at $x = 0$. For the voltage V externally applied to the electrodes, it is required that

$$V = \int_0^d E(x,t) dx, \quad (6)$$

where d is the distance between electrodes. From Eqs. (3) and (6), we obtain

$$E(0) = \frac{V}{d} - \frac{q}{d \varepsilon_0 \varepsilon_r(t)} \int_0^d [f_p(x,t) - f_n(x,t)] dx. \quad (7)$$

$E(0)$ represents the electric field at the electrode, i.e., $x = 0$. Let D_p and D_n be the diffusion coefficients of positive and negative mobile charges, respectively; similarly, let μ_p and μ_n be the mobilities. The current densities for positive and negative mobile charges $J_p(x,t)$ and $J_n(x,t)$ reduce to

$$J_p(x,t) = q \mu_p n_p(x,t) E(x,t) - q D_p \frac{\partial n_p(x,t)}{\partial x}, \quad (8)$$

$$J_n(x,t) = q \mu_n n_n(x,t) E(x,t) + q D_n \frac{\partial n_n(x,t)}{\partial x}. \quad (9)$$

Assuming that both electrodes block both mobile charges completely, the pertinent boundary conditions are

$$\mu_p n_p(x,t) E(x,t) - D_p \partial n_p(x,t) / \partial x = 0, \quad (10)$$

$$\mu_n n_n(x,t) E(x,t) + D_n \partial n_n(x,t) / \partial x = 0, \quad (11)$$

at $x = 0$ and $x = d$, respectively. The continuity equations are written as

$$q \frac{\partial n_p(x,t)}{\partial t} = - \frac{\partial J_p(x,t)}{\partial x}, \quad (12)$$

$$q \frac{\partial n_n(x,t)}{\partial t} = \frac{\partial J_n(x,t)}{\partial x}. \quad (13)$$

The PNPS model is represented by Eqs. (1)–(13). The difference from the PNP model is only $\varepsilon_r(t)$ given by Eq. (2). If we multiply both sides of Eq. (7) by $\varepsilon_0 \varepsilon_r(t)$, we obtain

$$\varepsilon_0 \varepsilon_r(t) E(0) = \frac{\varepsilon_0 \varepsilon_r(t) V}{d} - \frac{q}{d} \int_0^d [f_p(x,t) - f_n(x,t)] dx. \quad (14)$$

Equation (14) shows that the electric flux density at the electrode represented by the left hand side of the equation is composed of two factors: One is the first component on the right hand side that is the charge density that is supplied from an external power source to the electrode and the other is the second component that is the contribution of the redistributed ions between the electrodes. If the electric flux density is calculated assuming that $\varepsilon_r(t) = \varepsilon_s$ as in the PNP model, the charge density induced at the electrode becomes to be consisted of only the molecular polarizations, such as electronic, atomic, and dipole polarizations of the matrix material. However, if the external field is applied between the electrodes, the mobile charges are displaced in the bulk, and the excess charges near the electrodes induce countercharges to the electrodes through the external circuit. Since the quantity of the excess charges is determined by the space-charge polarization, the contribution of the space-charge polarization has to be included in the dielectric constant of Poisson's equation.

When the PNPS model is analyzed for the alternative current (ac) mode, the relative dielectric constant in the time domain given by Eq. (2) is transformed into the relative complex dielectric constant $\varepsilon_r^*(\omega) = \varepsilon_r'(\omega) - i \varepsilon_r''(\omega)$ in the frequency domain, where ω is the angular frequency and $i = \sqrt{-1}$. Its absolute value is expressed as [5]

$$|\varepsilon_r^*(\omega)| = \sqrt{[\varepsilon_s + \varepsilon_r'(\omega)]^2 + \varepsilon_r''(\omega)^2}, \quad (15)$$

where $\varepsilon_r'(\omega)$ and $\varepsilon_r''(\omega)$ are represented by Eqs. (36) and (37) of Ref. [5], respectively. Equation (15) has been used for Poisson's equation in the ac analysis of the PNPS model [5].

The authors of Ref. [2] have considered that the increase in the charge density at the electrodes, i.e., the generation of external current, is induced by only the adsorption of ions on the electrodes; however, this is not correct. If the ions are displaced in the matrix material by an external field, an external current is induced, and the charge density at the electrodes increases with the accumulation of the external charge even in the absence of the ionic adsorption. Therefore, Eqs. (15), (16), (22), and (23) of Ref. [2] do not lead to the correct values of the external current. The validity of Eq. (2) or (15) in the present Reply should be recognized by the fact that the measurement of the space-charge polarization is carried out by just measuring the external current. Although the necessity of Eq. (2) or (15) for analyzing experimental data is thus predicted naturally, it has never been discussed in the analysis using the PNP model until recently since the pioneering work on the space-charge polarization by Jaffé [6], Chang and Jaffé [7], Macdonald [8], and Friauf [9]. One of the reasons for this may be that the frequency-dependent curves of the complex dielectric constant predicted by the PNPS model tend to be largely suppressed by an interfacial capacity between the electrode and electrolyte for high ion concentrations and/or large distances between electrodes, which are the usual conditions for conventional electrochemical cells more than the electrolytic solution cells prepared in Ref. [1]. However, the PNPS model should enable one to understand more properly the frequency-dependent behaviors of the complex dielectric constant in low-frequency regions observed for electrolytic cells regardless of the ionic concentration and distance between electrodes.

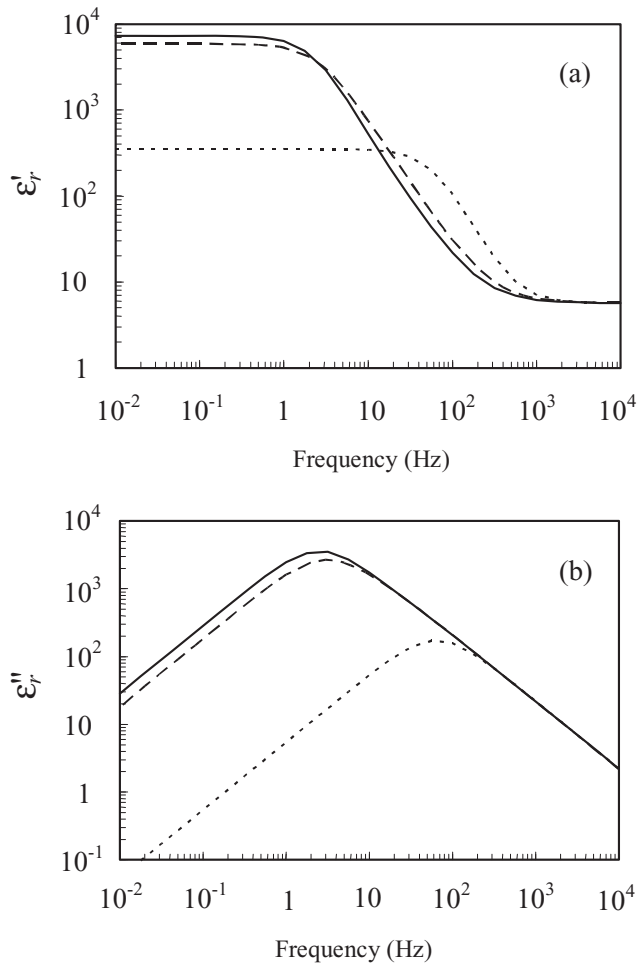


FIG. 1. Frequency dependence of (a) the dielectric constant and (b) the dielectric loss factor calculated by three kinds of models for the space-charge polarization. The solid lines, dotted lines, and dashed lines represent the values calculated by the NP, PNP, and PNPS models, respectively.

Finally, let us reconfirm the validity of the NP model for analyzing the space-charge polarization of the dilute electrolytic solution cells shown in Ref. [1]. The frequency dependences of the relative complex dielectric constant due to the space-charge polarization calculated by the NP, PNP, and PNPS models are shown in Fig. 1. In the figure, the relative dielectric constant ϵ_r' and the relative dielectric loss factor ϵ_r'' are calculated using Eqs. (26) and (27) of Ref. [1] for the NP model, using Eqs. (32) and (33) of Ref. [4] for the PNP model providing that $\epsilon_{r0} = 5.7$, that is, the dielectric constant

of chlorobenzene, and using Eqs. (36) and (37), respectively, of Ref. [5] for the PNPS model. Here, Eqs. (26) and (27) of Ref. [1] are equivalent to Eqs. (13) and (14), respectively, in Ref. [3]. Besides, the values of ϵ_r' and ϵ_r'' calculated by using the PNP model in Fig. 1 conform to the values that Barbero and Alexe-Ionescu have obtained using their PNP model [10]. In the calculation of Fig. 1, we assume that $D_p = D_n = 8.2 \times 10^{-10} \text{ m}^2/\text{s}$, $\mu_p = \mu_n = 3.2 \times 10^{-8} \text{ m}^2/\text{Vs}$, and $n_{p0} = n_{n0} = c_0 = 1.2 \times 10^{20} \text{ m}^{-3}$.

As shown in Fig. 1, although the frequency-dependent curves of ϵ_r' and ϵ_r'' calculated using the NP model are quite different from those calculated using the PNP model, they are very close to those calculated using the PNPS model. We have employed the simple electrolytic solution system for the measurement of ϵ_r' and ϵ_r'' in order to demonstrate the validity of the PNPS model [1,3,4]. The ionic constants of TBA⁺ and TPB⁻ have been well investigated by conductmetry in the past, and it has been known that they do not undergo solvation with any organic solvent molecule and their Stokes radii are both nearly 0.4 nm [11,12]. We have found that the difference between the PNPS and the NP models is around 10%–20% in terms of the Stokes radius of TBA⁺ and TPB⁻ ions showing 0.41 nm for the analysis using the PNPS model [4] and 0.35 nm for the analysis using the NP model [3]. On the other hand, if the same experimental data are analyzed using the PNP model, the Stokes radius becomes an extremely large value over 10 nm, and the ion density becomes an unrealistic value that is much larger than the doped concentration [4]. These results show the usefulness of the NP model for the PNPS model and the invalidity of the PNP model for analyzing the dilute electrolytic solution system. Furthermore, the $\omega^{-3/2}$ dependence of ϵ_r' [13–15] and the d^{-2} dependence of the relaxation frequency [16,17] observed elsewhere in the past can be well explained by the PNPS model or NP model rather than the PNP model [5,18].

Alexe-Ionescu *et al.* have pointed out in Ref. [2] that the analysis of the complex dielectric constant in Ref. [1] is carried out using the NP model assuming that TBATPB is completely dissociated in chlorobenzene solution, whereas TBATPB is not completely dissociated in the actual case. That is true; nevertheless, the assumption of the complete dissociation in the analysis is still valid for the present electrolytic solutions. It has been shown by Macdonald [8] and Paula *et al.* [19] that, if the diffusion coefficient and the mobility are the same between the positive and the negative ions, the dissociation from neutral centers and the recombination of the positive and negative ions have no impact on the ion density in the bulk solution. The other criticisms in Ref. [2] are basically originated from the problem of the internal electric field.

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