Asymptotic behaviors of the Poisson-Nernst-Planck model, generalizations and best adjust of experimental data

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ABSTRACT

We analyze the asymptotic behavior of the impedance (or immittance) spectroscopy response of an electrolytic cell in a finite-length situation obtained from the Poisson-Nernst-Planck (PNP) diffusional model and extensions by taking into account different surface effects. The analysis starts with the case characterized by perfect blocking electrodes and proceeds by considering non-blocking conditions on electrodes surface. We argue that the imaginary part of the impedance may be directly related to the boundary condition on the electrode surface, such as charge accumulation and/or transfer by electrochemical reaction or adsorption-desorption processes. We also compare the theoretical predictions with experimental data obtained for a weak electrolytic solution of $KClO_3$.

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1. Introduction

The continuous research and development of state-of-art materials and their electrochemical properties is a burgeoning area of science. It has contribute to a considerable progress in batteries [1–4], fuel cells [5–9], colloidal systems [10–13], oxygen-separation membranes [14,15], electrochemical sensors, functional polymers and biological tissues [16–19]. In this context, among the characterization methods often used, the impedance spectroscopy technique is quite popular. This is mainly due to the possibility of obtaining results related to complex variables (such as mass transfer and chemical reaction rates) via simple measurements.

Despite the deviations between experimental data and theoretical predictions, results from impedance spectroscopy are usually investigated in the framework of the Poisson–Nernst–Planck (PNP) model and/or equivalent circuits. These disagreements are especially remarkable in the low frequency limit, where the PNP and equivalent circuits with simple elements predict an asymptotic impedance $\mathcal{Z}$ characterized by a power-law dependence in the frequency ω with a unitary exponent (*i.e.*, $\mathcal{Z} \sim 1/(i\omega)$) but the experimental data usually exhibit a different power-law regime. These discrepancies are, therefore, strong motivation for investigating extensions/generalizations of the PNP model as well as of the equivalent circuits. For the PNP model, an important possibility is to consider that the diffusive dynamics of the ions is anomalous, which can be done via fractional derivatives [20]. Another relevant aspect to consider in the PNP model is the inherent complexity of the surface effects, which can be taken into account by generalizing the boundary conditions [21]. Regarding equivalent circuits, a typical extension is to use constant phase elements (CPE), in order to account for surface polarization effects [22–24].

In order to achive a suitable description for impedance spectroscopy data, it is crucial to understand the behavior of these generalized models in insightful situations, a task that has not been accomplished yet. An example is the low frequency limit, which is directly connected to the surface effects. Thus, one can find relationships between these behavior of the models and low frequency-relevant experimental aspects such as charge accumulation, charge transfer by electrochemical reaction, or adsorption–desorption processes. In order fill this gap, we devote this work to investigate the asymptotic behavior of the impedance calculated from extensions of the PNP models in the low frequency limit. We start by considering the case of perfect blocking electrodes, followed by the cases characterized by non-blocking electrodes. The influence of the physical chemistry properties of the model (such as mobility and number of particles) on the electrical response is obtained and compared with experimental data. These analyzes are explored in the Sec. 2 and 3, while the discussions and conclusions are presented in Sec. 4.

2. PNP Impedance Model and Boundary Conditions

We start by reviewing the Poisson-Nernst-Planck (PNP) diffusional model that is usually applied to describe the electrical response. We consider this model subjected to perfect blocking boundary, *i.e.*, $\mathcal{J}_{\pm}\left(\pm d/2, t\right) = 0$, where $\mathcal{J}_{\pm}(z, t)$ is the

drift-diffusion current density related to the positive (+) and negative (−) ions, with the electrodes placed at the positions $z = \pm d/2$. The PNP model is characterized by the continuity equation

$$\frac{\partial}{\partial t} n_{\pm}(z,t) = -\frac{\partial}{\partial z} \mathcal{J}_{\pm}(z,t), \tag{1}$$

in connection with

$$\mathcal{J}_{\pm}(z,t) = -\mathcal{D}_{\pm}\frac{\partial}{\partial z} n_{\pm}(z,t) \mp \frac{q\mathcal{D}_{\pm}}{k_B T} n_{\pm}(z,t)\frac{\partial V(z,t)}{\partial z}, \tag{2}$$

where $\mathcal{D}_+ = \mathcal{D}_- = \mathcal{D}$ is the diffusion coefficient (the same for positive and negative ions), $V(z,t)$ is the effective electric potential across a sample of thickness d, k_B is the Boltzmann constant, and T is the absolute temperature. Furthermore, the potential $V(z,t)$ satisfies the Poisson's equation

$$\frac{\partial^2}{\partial z^2} V(z,t) = -\frac{q}{\varepsilon} \left[n_+(z,t) - n_-(z,t) \right], \tag{3}$$

where ε is the dielectric coefficient of the medium (measured in ε_0 units). At this point it is worth mentioning that other models have also been employed for describing the electrical response of systems. Examples include the Debye-Falkenhagen model [25–27] (that is related to solving a partial differential equation for the potential) and models based on equivalent circuits such as the Randles-Ershler equivalent circuit [28,29].

We can investigate the electrical response of an electrolytic cell by solving these equations. To do so, a periodic potential with a very small amplitude is usually assumed to drive the system. This corresponds to the AC small-signal limit and produce a linear response of the system. Under these assumptions and after some calculations, we obtain the following expression for the impedance

$$\mathcal{Z}_B = \frac{\bar{z}}{i\beta^2\psi} \left[\frac{1}{\beta} \tanh\left(\mathcal{M}\beta\right) + i\mathcal{M}\psi \right], \tag{4}$$

with

$$\bar{z} = \frac{2\lambda_{\mathcal{D}}}{\omega_{\mathcal{D}}\varepsilon S} \qquad \text{and} \qquad \beta = \sqrt{1 + i\psi}. \tag{5}$$

Here, $\lambda_{\mathcal{D}} = \sqrt{\varepsilon k_B T/(2Nq^2)}$ is the Debye's screening length and S is the electrode area; $\psi = \omega/\omega_{\mathcal{D}}$, $\mathcal{M} = d/(2\lambda_{\mathcal{D}})$, and $\omega_{\mathcal{D}} = \mathcal{D}/\lambda_{\mathcal{D}}^2$ are constants. Notice that Eq. (4) corresponds to a linear response of the system and connects electric quantities with physical-chemical parameters.

We now focus on the asymptotic limit for low frequency of Eq. (4), where the diffusion and surface effects related to the dynamics of the electrolyte particles play an important role. In this limit, where $\psi \to 0$ (i.e., $\omega \to 0$), we have that $1/\beta \sim 1 - i\psi/2$ and can consider $d/\lambda_{\mathcal{D}} \gg 1$, implying that $\tanh(\mathcal{M}\beta)\sim 1$ (see Ref. [30] for more details). Under these assumptions, the main contributions for the real ($R_B = Re(\mathcal{Z})$) and imaginary ($X_B = Im(\mathcal{Z})$) parts of the impedance are

$$R_B \approx \frac{\lambda_{\mathcal{D}}^2 d}{S\mathcal{D}\varepsilon} \approx \text{const} \tag{6}$$

and

$$X_B \approx -2\frac{\lambda_{\mathcal{D}}}{\omega_{\mathcal{D}} S\varepsilon\psi}, \tag{7}$$

where the B subscript refers to the perfect blocking boundary condition (see the Appendix A for additional details).

Eqs. (6) and (7) essentially show that R_B and X_B exhibit a resistive and capacitive behavior. The resistive behavior is connected to the bulk effects. On the other hand, the capacitive behavior reflects the boundary conditions assumed on the surface of the electrodes, which only take in account charge accumulation and do not consider other effects such as adsorption–desorption processes and/or
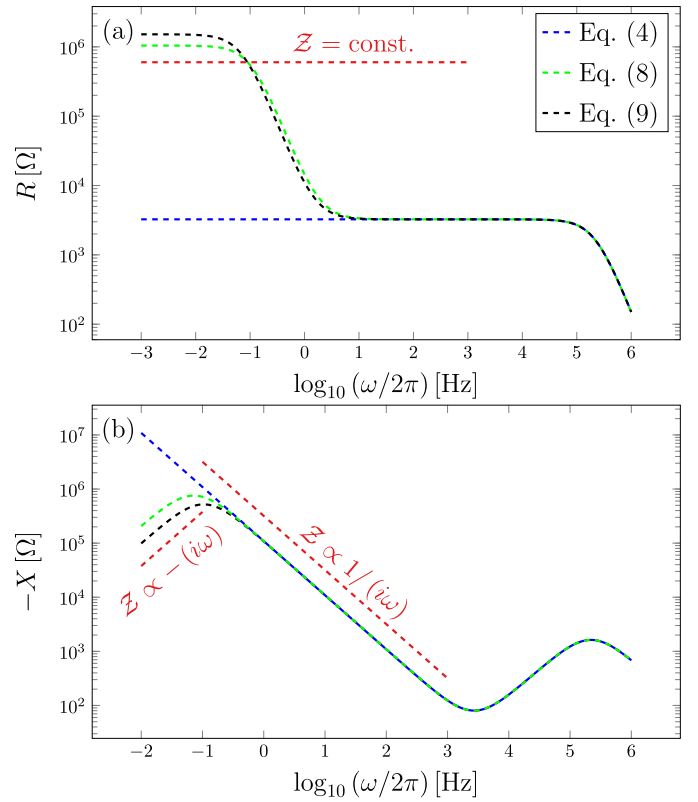
Fig. 1. The behavior of the real ($R = Re(\mathcal{Z})$) and imaginary ($X = Im(\mathcal{Z})$) parts of Eqs. (4), (8), and (9) is illustrated. For simplicity, we have considered $\mathcal{D} = 8 \times 10^{-9} \text{m}^2\text{s}^{-1}$, $\lambda_{\mathcal{D}} = 7.61 \times 10^{-8}\text{m}$, $\epsilon = 80\epsilon_0$, $q = 1.6 \times 10^{-19}\text{C}$, $S = 3.14 \times 10^{-4}\text{m}^2$, $d = 10^{-3}\text{m}$, $\kappa_{CJ} = 5 \times 10^{-8}\text{ms}^{-1}$, $\kappa_O = 2 \times 10^{9}(\text{V m s})^{-1}$. We also show red dashed lines as a guide for the asymptotic behavior exhibited by the impedance.

charge transfer. These behaviors are illustrated in Fig. 1, where the dependence of Eq. (4) on the frequency is shown.

At this point, it is very illustrative to perform a comparison with experimental data to comprehend the range of applicability of Eq. (4). A simple experimental scenario for the electrical response obtained from a weak electrolytic solution of KClO$_3$ ($\approx 2 \times 10^{-3}$ Mol L^{-1}) in Milli– Q deionized water (see Ref. [31,32] for more details on the experimental setup) is shown in Fig. 2 for the electrical impedance. It is evident that the PNP model with perfect blocking boundary conditions is not suitable to describe these experimental data in all range of frequencies. Notice, for instance, that the behavior the experimental data is not purely capacitive ($\mathcal{Z} \propto 1/(i\omega)$) as indicated by the dashed line in Fig. 2, a behavior not predicted by Eq.(4).

The PNP model has also been solved with different boundary conditions on the surfaces such as the Chang–Jaffe [33] ($\mathcal{J}_{\pm}\left(\pm d/2, t\right) = \pm \kappa_{CJ}\, n_{\pm}\left(\pm d/2, t\right)$) and the Ohmic [34] ($\mathcal{J}_{\pm}\left(\pm d/2, t\right) = \kappa_O\, E\left(\pm d/2, t\right)$). These boundary conditions are related to the conduction current across the electrode, i.e., charge transfer from the electrolyte to the electrode by electrochemical reactions. Under these hypotheses, the impedances for an electrolytic cell are given by

$$\mathcal{Z}_{CJ} = \bar{z}\frac{\mathcal{M}\psi\beta - i\left[1 + \mathcal{M}\mathcal{H}\left(1 + i\psi\right)\right]\tanh\left(\mathcal{M}\beta\right)}{\beta^2\left\{\psi\beta - i\mathcal{H}\left(1 + i\psi\right)\tanh\left(\mathcal{M}\beta\right)\right\}}, \tag{8}$$

and

$$\mathcal{Z}_O = \frac{1}{\beta^2}\bar{z}\mathcal{M}\left[1 - i\frac{1 - \psi_q}{\mathcal{M}\left(\psi - i\psi_q\right)\beta}\tanh\left(\mathcal{M}\beta\right)\right], \tag{9}$$