



A simple model of ac hopping surface conductivity in ionic liquids

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ABSTRACT

The boundary conditions proposed to discuss the charge exchange taking place in an ionic liquid in contact with non-blocking electrodes are reconsidered in a dynamic situation. Assuming that the variation of the bulk ionic current density depends linearly on the surface value of the ionic current density, the frequency dependence of the phenomenological parameter is determined. The analysis has been performed in the framework where the relaxation times are smaller than a maximum relaxation time τ_M , and that the response function is independent on the value of the relaxation time. Using simple physical considerations, an expression for the surface conductivity describing the ionic charge exchange at the electrode is obtained. According to our calculations, its frequency dependence is similar to that predicted for the electric conductivity in disordered materials when the mechanism is of the hopping type. From measurements of impedance spectroscopy, by the best fit of the experimental data, the temperature dependence of the hopping time, of the dc surface conductivity, and of the diffusion coefficient are derived. They are in good agreement with the theoretical predictions obtained with the random distribution of surface energy barrier.

1. Introduction

When an electrolytic cell is submitted to an external electric field, the ions move under the effect of the electric force toward the electrode of opposite sign. If the electrodes are blocking and the external field dc, the equilibrium state is the one where the total current, due to the diffusion and drift currents vanish identically. In this situation the ionic distribution coincides with the Boltzmann distribution [1,2]. This situation has been investigated by several researchers to understand the physical mechanisms taking place at the interface electrode-bulk solution [3,4]. In the dynamic case, where the external field depends on time [5,6], the electric response of the electrolytic cell can give information on the ionic carriers and of the role of the limiting electrodes [7,8]. In this case, the response of the cell depends on the properties of the electrodes. In particular, when the external field is a simple harmonic function of time, in the low frequency region the response of the cell strongly depends on the electrodes [9]. In the case where these can be assumed as blocking, the ionic currents vanish on it. In this framework, in the dc limit, the electric current in the external circuit vanishes identically. As it is well known, the case of blocking electrodes is an ideal case. In real electrodes there is an exchange of ionic charges on

the electrodes. To describe the electric response of an electrolytic cell to an external stimulus a macroscopic model based on the equations of continuity for the ions and on the Poisson equation for the electric potential across the cell is used. In this case, the properties of the electrodes enter the description as boundary conditions for the bulk partial differential equations. A review on the proposed boundary conditions for the problem under consideration is reported in [10]. In the same reference a full mathematical description of the response of an electrolytic cell to an ac external field is reported considering anomalous ionic diffusion with memory effects in the boundary conditions [10]. The analysis presented there can be generalized considering the surface effects [11,12]. The main merit of the general model presented in [10] is to underline that the dynamic form of the boundary conditions has not been a simple form. In the present paper we propose a theoretical description of non-blocking electrodes in dynamic situation. The goal of our paper is to consider in details the boundary conditions proposed by Chang and Jaffe [13], discussed in several publications [14], and to derive the dependence of the phenomenological parameter entering it on the external electric field frequency. We derive this functional dependence assuming that the relation between surface variation of the ionic bulk density and the density of surface ionic

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current across the electrode is linear. The parameter describing the charge transfer at the electrode is analyzed, assuming that the charge exchange from the bulk to the external circuit is of the hopping type. Using this model, it is possible to analyze the influence of the electrodes on the electrical response on the ionic solution to an external ac excitation. This kind of analysis is of fundamental importance in electrochemistry.

The theoretical model is presented in Section 2, whereas Section 3 is devoted to the experimental determination of the electric impedance spectra of the sample under investigation. In the same section we report the temperature dependence of the parameters of the model, and we compare them with the theoretical predictions obtained with the model based on the hopping mechanism. The conclusions are reported in Section 4.

2. Model

Long ago Chang and Jaffe proposed a model for non-ideal electrodes based on the assumption that the exchange of ionic charge on the electrodes is described by $j = \kappa \delta n$, where j is the surface density of ionic current and $\delta n = n_s - n_{eq}$ is the variation of the bulk density just in front of the electrode, n_s , with respect to the value corresponding to the thermodynamic equilibrium, n_{eq} , and κ is the reaction rate parameter at the reaction plane coinciding with the electrode [13]. This equation is similar to that used to describe the surface evaporation in a liquid [15]. Another manner to interpret this equation is that all the time there is a surface current, the surface value of the ionic bulk density changes with respect to the value of equilibrium. Using this point of view, the boundary condition proposed in [13] can be rewritten as $\delta n = \varphi j$, where $\varphi = 1/\kappa$. In this latter equation, j is considered the source of the variation of δn . In the dc case the quantity φ reduces to a constant, φ_s . In several problems devoted to the theoretical analysis of the impedance spectra, the quantity φ , or the corresponding κ , was assumed constant and equal to φ_s . This means that, in the dynamic case, the system responds immediately to variations of the external excitation. This is a rather crude approximation. In fact, as it is well known, in a dynamic problem, the time variation of δn follows the time variation of j with a certain delay, which depends on the properties of the system under consideration. Assuming that the system behaves in a linear manner, for what concerns the relation between δn and j , we rewrite $\delta n = \varphi j$ as

$$\delta n(t) = \varphi_s \int_0^\infty \Phi(u) j(t-u) du, \quad (1)$$

where $\Phi(u)$ is the response function of the system [16]. Decomposing $\delta n(t)$ and $j(t)$ in Fourier integrals from Eq. (1) we obtain $N(\omega) = \mathcal{R}(\omega) J(\omega)$ where $N(\omega)$ and $J(\omega)$ are Fourier transform of $\delta n(t)$, and $j(t)$, and

$$\mathcal{R}(\omega) = \varphi_s \left\{ \int_0^\infty \Phi(u) e^{-i\omega u} du \right\}. \quad (2)$$

The response function $\Phi(u)$ is assumed to be a superposition of simple relaxation phenomena related to the relaxation times $0 \leq \tau \leq \tau_M$, where τ_M is the maximum relaxation time [17]. It follows that

$$\Phi(u) = \int_0^{\tau_M} \frac{1}{\tau} G(\tau) e^{-u/\tau} d\tau \quad (3)$$

In this framework

$$\mathcal{R}(\omega) = \varphi_s \int_0^{\tau_M} \frac{G(\tau)}{1 + i\omega\tau} d\tau. \quad (4)$$

Assuming that all relaxation times in the range $(0, \tau_M)$ are equivalent and hence $G(\tau) = g$, from the condition of normalization on G we get $g = 1/\tau_M$. Consequently, from Eq. (4) we obtain

$$\mathcal{R}(\omega) = \varphi_s \frac{\log(1 + i\omega\tau_M)}{i\omega\tau_M}. \quad (5)$$

Rewriting the boundary condition of Chang-Jaffe in the form $j = \kappa \delta n$

the Fourier transform of the phenomenological parameter κ is

$$\kappa(\omega) = \kappa_s \frac{i\omega T}{\log(1 + i\omega T)}, \quad (6)$$

where $\kappa_s = 1/\varphi_s$.

A simple calculation allows to find a relation between κ and the surface conductivity describing the charge exchange on the electrode. According to Poisson equation, the electric field is related to the ionic bulk charge density by

$$\frac{dE}{dz} = \frac{q}{\varepsilon} [n(z) - n_{eq}], \quad (7)$$

valid in the case where the sample is a slab, and hence the problem is one-dimensional, and z -axis is normal to the limiting surfaces, coinciding with the electrodes. In Eq. (7) ε is the dielectric constant of the medium in which the ions are dispersed and q the ionic electric charge. From Eq. (7), written at the electrodes, we get

$$\left(\frac{dE}{dz} \right)_s = \frac{q}{\varepsilon} (n_s - n_{eq}), \quad (8)$$

where the subscript s means that the relevant quantities are evaluated on the electrode. In the case where the external difference of potential is so low that the system responds in a linear manner to the external excitation, the bulk electric field, E_b , is very small with respect to the surface electric field, E_s , and the electric field vanishes over a length of the order of Debye length, $\lambda = \sqrt{\varepsilon K_B T / (2n_{eq} q^2)}$, where $K_B T$ is the thermal energy. In this situation $(dE/dz)_s \sim (E_s - E_b)/\lambda \sim E_s/\lambda$, and from Eq. (8) we get

$$n_s - n_{eq} = \frac{\varepsilon}{q\lambda} E_s. \quad (9)$$

In this case the boundary condition $j = \kappa \delta n$ takes the form $j = s E_s$ where $s = \varepsilon \kappa / (q\lambda)$, proposed some years ago [18]. Since in the case under consideration ε and λ are frequency independent, the quantity s , playing the role of surface conductivity has the same frequency dependence of κ_s , and can be rewritten as

$$s(\omega) = s_0 \frac{i\omega\tau_M}{\log(1 + i\omega\tau_M)}. \quad (10)$$

This expression is similar to the expression proposed to describe the conductivity due to hopping mechanism in a disordered medium.

3. Dielectric measurements

In order to validate the model, the dielectric response of an electrolytic cell submitted to an ac external electric field of small amplitude has been investigated by means of the impedance spectroscopy technique. The measurements were performed with a Potentiostat/galvanostat (Methrom, model 128N, fitted with a frequency response analyzer module), in the frequency range of 1 MHz–1 mHz and amplitude of the applied signal 10 mV. The cells having the shape of a slab delimited by transparent FTO electrodes, were filled with the ionic liquid crystal electrolyte 1-dodecyl-3-methylimidazolium iodide (C12), of thickness $d_1 = 25 \mu\text{m}$, surface area $S = 10^{-4} \text{m}^2$. Impedance measurements were carried out at the following temperatures, in °C, 25, 30, 35, 40, and 45 [19].

A preliminary experimental investigation of the conduction properties of this material has been reported in [19]. In that publication, the analysis of the dielectric spectra was done assuming that the cell is equivalent, from the electric point of view, to a parallel of a resistance, R_0 , and a condenser C_0 . The resistance was supposed to take into account all dissipative phenomena. It was not separated in bulk and surface contributions, and neither was for the capacitance. With this assumption, it was possible to fit in a reasonable manner the spectra for the real, Z' , and imaginary, Z'' , parts of the electric impedance, as well as the parametric plot of Z'' versus Z' . From the temperature

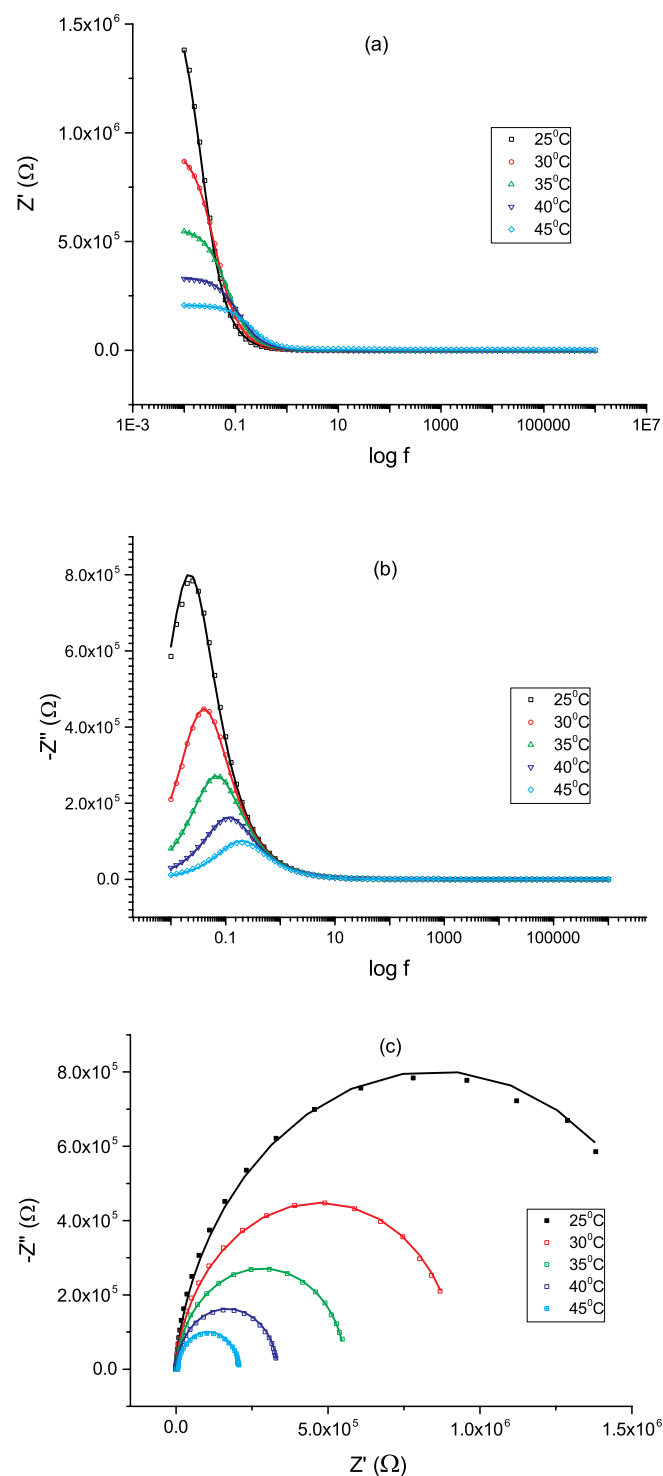


Fig. 1. Frequency dependence of the real part, Z' , a, and of the imaginary part, Z'' , for the considered sample, for the temperatures indicated in the insert. Parametric plot of Z' versus Z'' , c. Continuous curve are the best fit obtained using the PNP model with Chang-Jaffe boundary conditions, with the phenomenological coefficient $\kappa = \kappa(\omega)$ given by the model presented in the text.

dependencies of Z' and Z'' obtained experimentally, we derived $R_0 = R_0(T)$ and $C_0 = C_0(T)$. The temperature dependence of R_0 was regular, indicating a thermally activated mechanism for the electric conduction. On the contrary, $C_0 = C_0(T)$ was nearly independent on T , and from our experimental data it was impossible to derive a clear indication on the mechanisms responsible for the electric response of

the cell to the external voltage. This was related to the simple model used for the description. In the present paper our goal is the analysis of the data, partially presented in [19], with a physical model based on a particular mechanism for the charge exchange on the electrode, where the bulk of the liquid crystal is described in terms of the standard PNP model.

In Fig. 1 are reported the spectra of Z' , a, and Z'' , b, of the electric impedance of the cell for the explored frequency range $10^{-2} - 10^6$ Hz and for the five values of the temperature investigated. The parametric plot of the Z' versus Z'' is reported in c.

The electric impedance of a sample in the shape of a slab of thickness d and surface area S , can be easily determined in the framework of PNP model with Chang-Jaffe boundary conditions [9]. Assuming that the ions are identical in all the aspects, except for the sign of the electric charge, with a diffusion coefficient in the liquid equal to D , the impedance of the cell is given by

$$Z = R_\infty \frac{M\Omega\sqrt{1+i\Omega} - i[1+MH(1+i\Omega)] \tanh(M\sqrt{1+i\Omega})}{M(1+i\Omega)[\omega\sqrt{1+i\Omega} - iH(1+i\Omega) \tanh(M\sqrt{1+i\Omega})]} \quad (11)$$

where $R_\infty = \lambda^2 d / (\epsilon DS)$, and $M = d / (2\lambda)$. In Eq. (11) $\Omega = \omega / \omega_D$ where $\omega_D = D / \lambda^2$ is Debye angular frequency, and $H = \kappa \lambda / D$ [9]. The assumption that positive and negative ions have the same diffusion coefficients is valid only for solutions like NaCl in water. In general, the diffusion coefficients of the positive, D_p , and negative, D_n , ions differ. However, in the frequency range explored by us the effective diffusion coefficient is the free diffusion coefficient defined as $D_f = (D_p + D_n) / 2$. It follows that, in Eq. (11) D is actually D_f .

The continuous curves in Fig. 1 are the best fit obtained with Eq. (11), where $\kappa = \kappa(\omega)$ is given by Eq. (6).

From the simultaneous best fit of the of $Z' = Z'(f)$ and $Z'' = Z''(f)$ for the temperature explored, we have obtained the temperature dependence of the maximum relaxation time τ_M and of κ_s , shown in Figs. 2 and 3, respectively. Assuming that Chang-Jaffe mechanism for the charge exchange on the electrode is governed by a hopping mechanism [20,21], the maximum relaxation time τ_M is given by

$$\tau_M = \tau_0 \exp\left(\frac{U_p}{K_B T}\right), \quad (12)$$

where U_p is the maximum potential barrier height at the percolation threshold and τ_0 a scale factor [22,23]. Fitting the experimental data reported in Fig. 2 for τ_M by means of Eq. (12) we get for $U_p = 0.87$ eV,

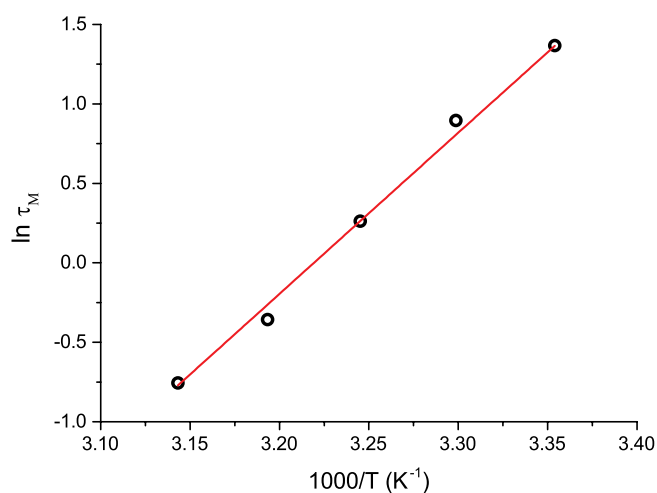


Fig. 2. Temperature dependence of the maximum relaxation time τ_M . The continuous curve is the best fit obtained in the framework of a hopping model, discussed in the text. From the best fit the maximum value of the potential barrier height at the percolation threshold is found to be $U_p = 0.87$ eV.

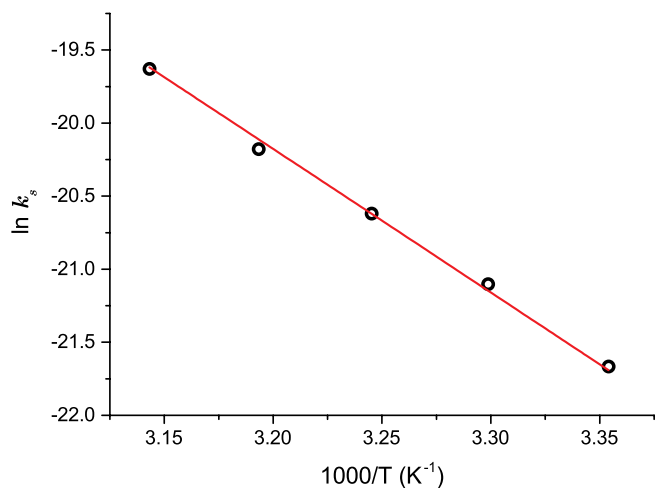


Fig. 3. Temperature dependence of the phenomenological parameter κ_s entering in Chang-Jaffe boundary conditions. The continuous curve has been obtained assuming that the surface conductivity responsible for the charge exchange across the electrode is of the hopping type. From the best fit of the experimental data we get again $U_p = 0.87$ eV, as from the best fit of the maximum relaxation time. This agreement supports the validity of the proposed theoretical model for the surface conductivity.

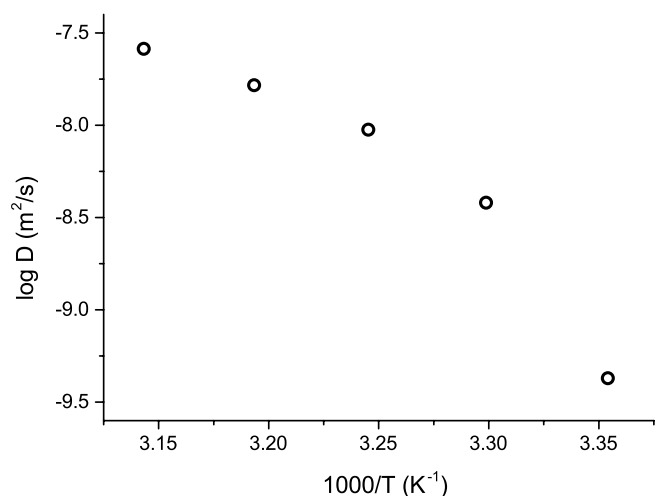


Fig. 4. Temperature dependence of the diffusion coefficient of the ions. Best fit values obtained from the impedance spectroscopy data in the framework of a hopping model, discussed in the text.

of the same order of magnitude reported in [22]. As it follows for Fig. 2, $\log \tau_M$ is a linear function of $1/T$. This functional dependence indicates that the conduction across the electrode is a thermally activated process. For what concerns the dependence of κ_s on the temperature it is necessary to take into account the discussion reported at the end of the previous section, according to which $s \propto \kappa_s$. Assuming that the surface conductivity describing the charge exchange at the electrode is of the hopping type, we get [22,24]

$$\kappa_s = \beta \frac{U_p}{K_B T} \exp\left(-\frac{U_p}{K_B T}\right), \quad (13)$$

where β is temperature independent. The best fit of the experimental values of $\kappa_s = \kappa_s(T)$ reported in Fig. 3 by means of Eq. (13) is shown by the continuous curve in the same figure.

From the impedance spectroscopy measurements, the temperature dependence of the self-diffusion coefficient of the ions is obtained and shown in Fig. 4. The same dependence was reported in the literature analyzing the charge transport in ion-conducting disordered media. The

process can be interpreted in terms of charge hopping in a randomly varying surface energy barriers [25,26].

4. Conclusions

We have investigated the charge exchange across the electrode in contact with an electrolytic solution. We assumed that the kinetic equation describing the charge transfer from the bulk to the external circuit connects the surface density current to the ionic bulk density variation, involving a phenomenological parameter typical of the interface electrode-electrolytic solution. In this framework, in the linear approximation of the kinetic equation, we determined the frequency dependence of the phenomenological parameter entering the kinetic equation at the electrode. To validate the model, we have performed impedance spectroscopy measurements in the frequency range $10^{-2} - 10^6$ Hz for temperatures ranging between 25 °C and 45 °C. From the best fit of the spectra of the real and imaginary parts of the electric impedance of the cell performed with the PNP model with our kinetic equation, the dc value of the phenomenological parameter as well as of the maximum relaxation time have been obtained. The temperature dependencies of the obtained parameters indicate that it is a thermally activated process. Our experimental temperature dependencies can be well interpreted assuming that the charge exchange at the electrode is of hopping type.

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