Influence of the Generation-Recombination Term on the Dielectric Relaxation in an Electrolytic Cell

Ioannis Lelidis * and Giovanni Barbero

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Article

Influence of the Generation-Recombination Term on the Dielectric Relaxation in an Electrolytic Cell

G. Barbero [1,2] and I. Lelidis [3,*]

[1] Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy
[2] Istituto dei Sistemi Complessi (ISC–CNR), Via dei Taurini, 19, 00185 Rome, Italy
[3] Department of Condensed Matter Physics, Faculty of Physics, National and Kapodistrian University of Athens, Panepistimiopolis, Zografos, Athens 157 84, Greece
* Correspondence: ilelidis@phys.uoa.gr

Abstract: We investigate the influence of the generation-recombination term on dielectric relaxation in an electrolytic cell shaped like a slab, bounded by two parallel blocking electrodes. We show that, in the adiabatic limit, valid when the reaction time is much longer than the dielectric relaxation time, the electric current in the external circuit does not result from a simple relaxation mechanism. Instead, it is characterized by a short relaxation time associated with dielectric relaxation and a long relaxation time related to the dissociation process.

Keywords: ion generation-recombination; dielectric relaxation; electrolytic cell; reaction time; blocking electrodes; displacement current

1. Introduction

Relaxation phenomena in a electrolytic cell submitted to a step-like electric field are usually investigated using the Poisson-Nernst-Planck model, which is based on the continuity equations and Poisson's equation that relates the electric field to the electric charge of ionic origin. The generation-recombination term [1] in the continuity equations is usually considered in the determination of the impedance spectroscopy of cells subjected to periodic excitations of small amplitude [2–5]. However, it is neglected in the analysis of relaxation phenomena in electrolytic cells subjected to a step-like external electric field. The goal of the present paper is to investigate the role of the generation-recombination term in the dielectric relaxation phenomenon of an electrolytic cell limited by blocking electrodes. We assume that ions are generated through the decomposition of neutral particles via the reaction mechanism $A \rightleftharpoons B^+ + C^-$, with dissociation and recombination coefficients as described in standard kinetic models. The reaction could be optically induced, as in semiconductors, or driven by another external energy source. Our focus is on the relaxation of the electric current in the circuit, which is the quantity experimentally observable. The paper is organized as follows: In Sect.II the time dependence of the bulk ion density generated by the dissociation of neutral particles is determined. In Sect.III, the time dependence of the Debye length, Debye time and dielectric relaxation time are investigated. Moreover, the validity of the adiabatic approximation is discussed. Section IV is devoted on the analysis of current relaxation in a circuit containing the electrolytic cell limited by blocking electrodes. Finally, the conclusions are reported in Sect.V.

2. Model

Let us consider an insulating liquid containing, at $t = 0$ a uniform distribution of neutral impurities that can produce ions by means of the reaction $A \rightleftharpoons B^+ + C^-$. The reaction could be initiated for instance through exposure to light or heat or interaction with another external source of

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energy. The evolution of the bulk density of the neutral n_n, positive, n_p and negative, n_m, particles is described by the continuity equations [1]

$$\begin{aligned} \frac{\partial n_n}{\partial t} &= -\nabla \mathbf{j}_n - k_d n + k_a n_p n_m, && (1)\\ \frac{\partial n_p}{\partial t} &= -\nabla \mathbf{j}_p + k_d n - k_a n_p n_m, && (2)\\ \frac{\partial n_m}{\partial t} &= -\nabla \mathbf{j}_m + k_d n - k_a n_p n_m, && (3) \end{aligned}$$

where k_d and k_a are the dissociation and association coefficients respectively. The dissociation coefficient is expected to depend on the energy of the source that induces the decomposition of the neutral particles. In (1,2,3) the current densities $\mathbf{j}_n$, $\mathbf{j}_p$ and $\mathbf{j}_m$ are given by

$$\begin{aligned} \mathbf{j}_n &= -D_n \nabla n_p,\\ \mathbf{j}_p &= -D_p \nabla n_p + \mu_p n_p \mathbf{E},\\ \mathbf{j}_m &= -D_m \nabla n_m - \mu_m n_m \mathbf{E}. && (4) \end{aligned}$$

In (4) D_n, D_p, D_m are the diffusion coefficients of the particles in the insulating liquid, μ_p and μ_m the mobilities of the positive and negative ions respectively, and $\mathbf{E}$ the local electric field, related to the bulk densities of ions by the Poisson equation

$$\nabla \cdot \mathbf{E} = \frac{1}{\varepsilon} q\,(n_p - n_m), \qquad (5)$$

where ε is the dielectric constant of the solvent in which the ions are dispersed. For a thick cell in the shape of a slab, limiting our analysis to an infinite medium in equilibrium, the drift diffusion phenomena can be neglected. In this case the medium is globally and locally electrically neutral. Therefore, assuming $n_p = n_m = p$ and writing $n_n = n$, (1,2,3), are cast in the form

$$\begin{aligned} \frac{dn}{dt} &= -k_d\, n + k_a\, p^2, && (6)\\ \frac{dp}{dt} &= k_d\, n - k_a\, p^2. && (7) \end{aligned}$$

We assume that for $t = 0$ the impurities have an initial bulk density N_0, and that the system evolves towards an equilibrium state as $t \to \infty$, under the effect of the external source inducing the decomposition of the neutral particles. This implies that

$$n(0) = n_0,\ p(0) = 0,\ \lim_{t\to\infty} n(t) = N,\ \lim_{t\to\infty} p(t) = P. \qquad (8)$$

From (6,7) it follows that

$$\frac{d(n+p)}{dt} = 0, \quad n(t) + p(t) = N_0 \qquad (9)$$

Consequently, from (7) we get

$$n(t) = \frac{1}{k_d}\left(\frac{dp}{dt} + k_a\, p^2\right) \qquad (10)$$

By substituting (10) into (6) we obtain

$$\frac{d^2 p}{dt^2} + 2\,k_a\, p\,\frac{dp}{dt} + k_d\,\frac{dp}{dt} = 0, \qquad (11)$$

from the latter it follows that the quantity

$$\frac{dp}{dt} + k_a\, p^2 + k_d\, p = c \qquad (12)$$

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is time independent. Hence, for (8), the integration constant c can be expressed in terms of the equilibrium value of p, denoted by P. We have

$$c = k_a\, P^2 + k_d\, P, \tag{13}$$

and the ordinary differential equation (12) becomes

$$\frac{dp}{dt} = k_a\,(P - p)\,[P + p + (k_d/k_a)]. \tag{14}$$

Integrating (14) with the initial condition $p(0) = 0$, we obtain

$$p(t) = P\,[P + (k_d/k_a)]\,\frac{1 - \exp(-t/\tau)}{(k_d/k_a) + P\,[1 + \exp(-t/\tau)]} \tag{15}$$

where the relaxation time τ is given by

$$\tau = \frac{1}{k_a[2P + (k_d/k_a)]} \tag{16}$$

The bulk densities of the neutral particles and ions in the equilibrium state, N and P respectively, are given by (6,7). Taking into account the condition $n(t) + p(t) = N_0$, these equations can be rewritten as

$$-k_d\, N + k_a\, P^2 = 0, \tag{17}$$

$$N + P = N_0, \tag{18}$$

with the solution

$$P = -\frac{k_d}{2k_a} + \sqrt{\left(\frac{k_d}{2k_a}\right)^2 + \frac{k_d}{k_a}\,N_0}. \tag{19}$$

The relaxation time (16), in terms of the dissociation and association coefficients k_d and k_a is expressed as

$$\tau = \frac{1}{\sqrt{k_d(k_d + 4k_a N_0)}}. \tag{20}$$

In the framework of the present model, the dissociation parameter, defined by $\rho = P/N_0$, is

$$\rho = -\frac{k_d}{2N_0k_a} + \sqrt{\left(\frac{k_d}{2N_0k_a}\right)^2 + \frac{k_d}{N_0k_a}} \tag{21}$$

It is possible to express k_a and k_d in terms of τ and ρ. A simple calculation gives

$$k_a = \frac{1 - \rho}{\rho\tau(2 - \rho)N_0}, \quad \text{and} \quad k_d = \frac{\rho}{\tau(2 - \rho)}. \tag{22}$$

In term of ρ and τ the time evolution of the ionic density is

$$p(t) = \rho\, N_0\, \frac{1 - \exp(-t/\tau)}{1 + (1 - \rho)\,\exp(-t/\tau)}, \tag{23}$$

The time evolution of the neutral particles (not dissociated) is given by $n(t) = N_0 - p(t)$, and by means of (23) it is found to be

$$n(t) = N_0\, \frac{1 - \rho + \exp(-t/\tau)}{1 + (1 - \rho)\,\exp(-t/\tau)} \tag{24}$$

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It could be of some interest the time t^* for which $n(t^*) = p(t^*)$. A simple calculation gives

$$t^* = \tau \log\left(\frac{\rho+1}{2\rho-1}\right), \tag{25}$$

from which it follows that t^* exists only if $\rho > 1/2$, as expected. In Figure 1 it is shown the time dependence of p/N_0 and n/N_0 for $\rho = 0.8$ and $\rho = 0.3$, and the same τ.

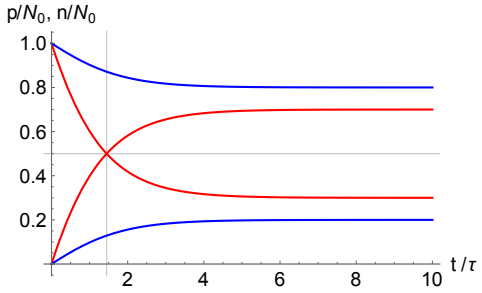

Figure 1. Reduced concentrations p/N_0 and n/N_0 vs reduced time, t/τ, for two values of the dissociation parameter ρ. Red curves, $\rho = 0.7$, blue curves, $\rho = 0.2$. The chemical reaction characteristic time τ is assumed the same for both ρ values. The vertical line indicates t^*.

3. Debye Length and Dielectric Relaxation Time

The Debye length [6] for the simple case of a single type of mobile ions with bulk density, p, is defined as $\Lambda = \sqrt{\varepsilon v_{\rm th}/(pq)}$, where $v_{\rm th} = k_B T/q$ is the thermal voltage. In standard problems, Λ is of the order of the thickness of the layer where the ions are confined when the cell is subjected to a small external potential difference, of the order of $v_{\rm th}$. The Debye relaxation time is defined by $\tau_D = \Lambda^2/D$ and the dielectric relaxation time [7] by $\tau_{\rm diel} = \Lambda d/(2D)$. The quantity $\tau_{\rm diel}$ is related to the relaxation of the initial distribution of ions, under the effect of the external field, and it is rather important for applications. In the case under consideration, since $p = p(t)$ these quantities are time dependent. We indicate by

$$f(t) = \frac{1-\exp(-t/\tau)}{1+(1-\rho)\,\exp(-t/\tau)}, \tag{26}$$

and rewrite (23) as $p(t) = Pf(t)$. The quantities of interest are

$$\Lambda(t) = \frac{\Lambda_{\rm eq}}{\sqrt{f(t)}},\ \tau_D(t) = \frac{\tau_{D,\rm eq}}{f(t)},\ \tau_{\rm diel}(t) = \frac{\tau_{\rm diel,eq}}{\sqrt{f(t)}}, \tag{27}$$

where

$$\Lambda_{\rm eq} = \sqrt{\frac{\varepsilon v_{\rm th}}{Pq}},\quad \tau_{D,\rm eq} = \frac{\Lambda_{\rm eq}^2}{D},\quad \tau_{\rm diel,eq} = \frac{\Lambda_{\rm eq} d}{2D}, \tag{28}$$

are the usual quantities evaluated for the equilibrium density of mobile ions at equilibrium, P.

The bulk density of mobile ions, $p(t)$, changes with time t with a characteristic time τ, and their confinement with $\tau_{\rm diel}(t)$ [8–10]. If $\tau_{\rm diel}(t) \ll \tau$, the system follows adiabatically the variation of $p(t)$. This implies that p can be treated as time-independent in the analysis. This assumption is valid for $t \gg t_c$ where

$$t_c = \tau \log\left(\frac{(1-\rho)+(\tau/\tau_{\rm diel,eq})^2}{(\tau/\tau_{\rm diel,eq})^2-1}\right) \tag{29}$$

In the case in which $\tau \gg \tau_{\rm diel,eq}$, t_c is very small, and the adiabatic approximation can be used for the analysis of the relaxation phenomena in a real system. In Figure 2 is shown the time dependence of the dielectric relaxation time in the presence of the considered generation-recombination term.

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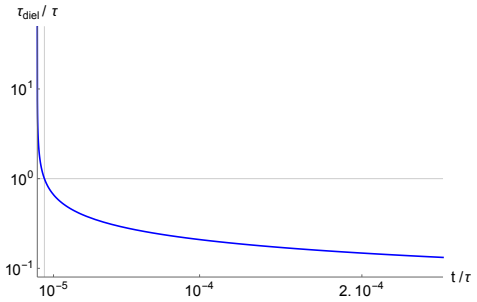

Figure 2. Time dependence of the dielectric relaxation time τ_{diel} in units of τ. The vertical line indicates the critical time t_c/τ, such that for $t \gg t_c$ the adiabatic approximation works well. The horizontal line indicates $\tau_{\text{diel}} = \tau$. The physical parameters used for the simulation are $D = 10^{-10}$ m^2/s, $N_0 = 10^{21}$ m^{-3}, $\rho = 0.1$, $\tau = 120$ s, and $\varepsilon = 2.4 \times \varepsilon_0$, typical for magnetic particles in kerosene.

4. Electric Current Relaxation in a Cell Limited by Blocking Electrodes

We recently investigated the dielectric relaxation in an electrolytic cell limited by blocking electrodes [11] containing a bulk density of impurities that are completely dissociated. According to the analysis presented in [11], when the cell is subjected to a small dc external potential difference of amplitude V_0, the equations of the Poisson-Nernst-Planck model can be linearized. The equilibrium distributions are practically reached after a few relaxation times, τ_{diel}. In particular, the electric potential profiles tends to

$$V(z) = \frac{1}{2} V_0 \frac{\sinh(z/\Lambda)}{\sinh[d/(2\Lambda)]}. \tag{30}$$

For $t \gg \tau_{\text{diel}}$, the time dependence of the potential profile is well described by

$$V(z,t) = V(z)\left(1 - e^{-t/\tau_{\text{diel}}}\right). \tag{31}$$

In the adiabatic approximation, (30) and (31) remain valid, but it is necessary to replace Λ and τ_{diel} with $\Lambda(t)$ and $\tau_{\text{diel}}(t)$ given by (27). It follows that $V(z,t)$ depends on t directly, and via the quantities $\Lambda(t)$ and $\tau_{\text{diel}}(t)$. In the external circuit, if the electrodes are blocking, the electric current is just a displacement current, related to the time variation of the surface electric field E_s. From (30) the profile of the electric field is given by

$$E(z,t) = -\frac{V_0}{2\Lambda} \frac{\cosh(z/\Lambda)}{\sinh[d/(2\Lambda)]}. \tag{32}$$

In particular the surface electric field is

$$E_s(t) = E(d/2,t) = -\frac{V_0}{2\Lambda} \coth\left(\frac{d}{2\Lambda}\right). \tag{33}$$

The related displacement current is then

$$i = \varepsilon \frac{dE_s}{dt}. \tag{34}$$

In Figure 3a is shown the time dependence of the electric current in the external circuit containing the electrolytic cell. As evident from Figure 3a, the current dependence is characterized by a short relaxation time associated with dielectric relaxation and a long relaxation time related to the generation-recombination term τ. For $t \gg \tau_{diel}$, an apparent plateau is observed. The values of the corresponding currents are proportional to the applied potential difference, as evident from Eq.s(33,34).

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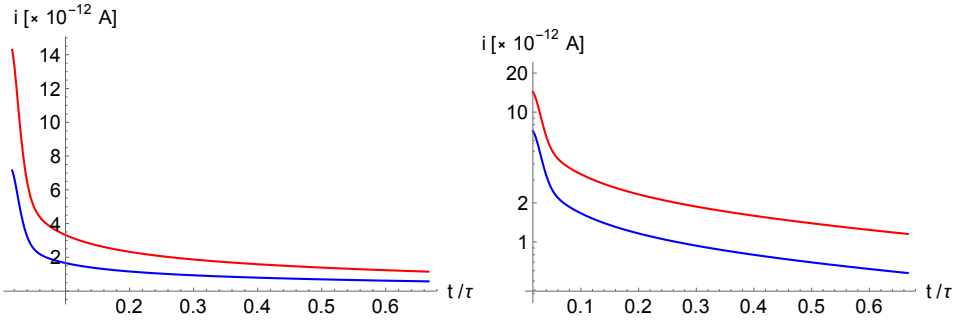

Figure 3. Time dependence of the displacement current, i, in an electrolytic cell in the presence of a generation-recombination term, evaluated in the adiabatic approximation, for two values of the applied potential difference: red curve, $V_0 = 60$ mV, blue curve, $V_0 = 30$ mV, in panel (a). In panel (b), the relaxation of the current is shown on a logarithmic scale. It is evident from the plot that there are two distinct relaxation times. The physical parameters are the same as those in Figure 2, and the geometrical parameters of the cell are $d = 10^{-4}$ m and $S = 10^{-4}$ m^2.

5. Conclusions

We have investigated the role of the generation-recombination term in the dielectric relaxation of an electrolytic cell with blocking electrodes. In our analysis, we assumed that the characteristic time of the chemical reaction, which describes the decomposition of the neutral particles that generate the ions, is much longer than the dielectric relaxation time corresponding to the equilibrium state. Within this framework, the adiabatic approximation, in which the system is always considered to be very close to equilibrium for a given ion density, we have evaluated the electric field profile and the corresponding displacement current. This current originates from the time variation of both the bulk ion density and the dielectric relaxation time. According to our results, the time relaxation of the electric current in the external circuit is characterized by two relaxation times, which are significantly different from each other and are related to the two different sources of the current.

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