Annuaire de l'Université "St. Kliment Ohridski", Faculté de Physique, 98, 2005

ELECTROSTATIC FORCES IN AN ELECTROLYTIC CELL WITH BLOCKING ELECTRODES

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Николай Танковски, Евгени Сираков, Клаус Бернер. ЕЛЕКТРОСТАТИЧНИ СИЛИ В ЕЛЕКТРОЛИТНА КЛЕТКА С БЛОКИРАНИ ЕЛЕКТРОДИ

Използван е алгоритъм, при който една от променливите в нелинейните членове на уравненията е изместена във времето с една стъпка. Анализирани са преходните процеси в електролитна клетка, на която се подава стъпалообразно напрежение. Клетката се състои от успоредни плоски електроди, изолирани с тънки диелектрични слоеве, което прави преминаването на заряди през електродите невъзможно. Еволюцията във времето на йонните заряди, на йонните потоци и на разпределението на електричното поле е оценена и анализирана. Електростатичните сили, действащи на електродите, са оценени с помощта на енергиен подход.

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A numerical algorithm is used, based on a small, one time-step shift for one of the variables in the nonlinear terms of the governing equations. The transient processes in an electrolytic cell, driven by a step electric voltage, are numerically analyzed. The cell comprises parallel plate electrodes, isolated by thin dielectric layers to prevent charge transfer through the electrodes. The time evolution of the ion charge densities, of the ion fluxes and of the electric field distribution has been evaluated and analyzed. Energy approach has been used to evaluate the electrostatic forces acting upon the electrodes.

Keywords: electrolyte, electroacoustic effect, electrostatic forces
PACS number: 82.45.Hk, 61.20.Lc, 61.20.Qg, 02.60.Cb

1. INTRODUCTION

In a series of experiments it has been shown that when an a. c. external, electric field is applied to a slab of parallel plate electrodes with electrolytic solution between them, mechanical forces occur which set into oscillating motion a mobile electrode [1-4]. In this way the cell can be used as an ultrasound transducer or the generated acoustic signals can be analyzed to retrieve information about the electrolyte solution. However, a theoretical basis is needed for the interpretation of the experimental results. The governing partial differential equations describing the dynamics of the ion charge densities and of the electric field distribution in the cell are nonlinear and it is principally impossible to obtain analytical solution in a closed form. Numerical analyses of the problem have been employed, in which different approaches have been used. The nonlinear equations can be approximated with the help of fitting parameters [5,6] or finite element methods can be used[7]. A simple numerical algorithm [8] is applied in the present work, which allows us to analyze the dynamics of the ion fluxes and the total current in the cell in response to a step voltage, but also to evaluate the electrostatic forces acting at the electrodes of the cell.

2. GENERAL EQUATIONS

We shall consider an electrolytic cell with parallel-plate electrodes, which is presented schematically in Fig. 1. The metal electrodes are covered with thin dielectric layers, so no charge transfer occurs through the interface metal-electrolyte and the electrodes are blocking. Since the electrode diameter is much larger than the interelectrode distance L we can assume that all characteristic variables are one dimensional, varying solely along the coordinate x, normal to the electrodes.

In order to evaluate the electrostatic forces we have to define the time dependence of the ion charge densities $n(x,t)$ and $p(x,t)$, but also the time evolution of the corresponding space distribution of the electric potential $Y(x,t)$ and of the electric field strength $E(x,t)$. Another measurable quantity, deserving evaluation is the total current comprising the Faradaic flux components of the two types of ion charges and the displacement current

$$I = Z_p e J_p - Z_n e J_n + \frac{\varepsilon}{4\pi}\frac{\partial E}{\partial t}, \tag{1}$$

where the positive and negative ion flux densities J_p and J_n are defined by the Nernst-Planck equations as follows:

$$\begin{aligned} J_p &= D_p \frac{\partial p}{\partial x} - \mu_p p E, \\ J_n &= D_n \frac{\partial n}{\partial x} + \mu_n n E. \end{aligned} \tag{2}$$

The coefficients μ_i, D_i, and Z_i denote the mobility, the diffusion coefficient and the valence of the positive ($i = p$) and negative ($i = n$) ions correspondingly.

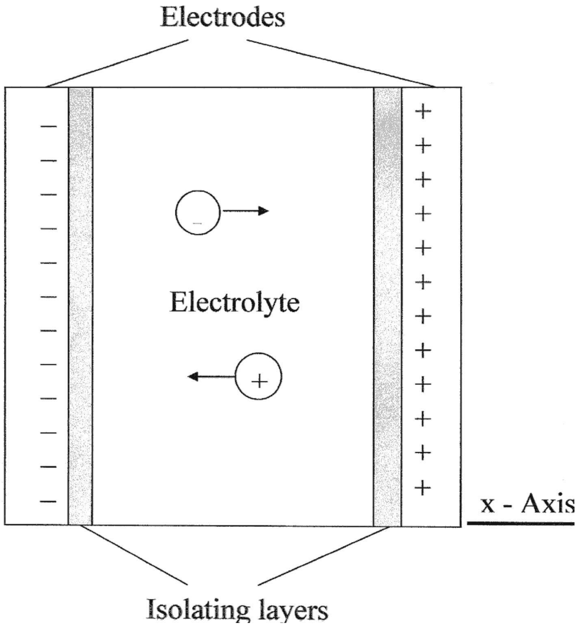


Fig. 1. A scheme of the electroacoustic cell

Dimensionless variables have been obtained by applying the following normalization relations:

$$\begin{aligned} n^* &= \frac{nZ_n}{c_0}; & p^* &= \frac{pZ_p}{c_0}; & E^* &= (\frac{eL_D}{kT})E; \\ x^* &= \frac{x}{L_D}; & t^* &= \frac{t}{\tau_D}; & I* &= \frac{L_D I}{kTc_0(\mu_n + \mu_p)} , \end{aligned} \tag{3}$$

where $c_0 = Z_n n_0 = Z_p p_0$ is the uniform, unperturbed charge concentration obeying the overall electroneutrality condition, k is the Boltzmann constant, T is the temperature, L_D is the Debye length and τ_D is the dielectric relaxation time, defined by the following formulae:

$$L_D^2 = \frac{\varepsilon kT}{4\pi e^2(Z_n^2 n + Z_p^2 p)} = \frac{\varepsilon kT}{4\pi e^2 c_0(Z_n + Z_p)}, \tag{4}$$

$$\tau_D = \frac{\varepsilon}{4\pi e(Z_n n\mu_n + Z_p p\mu_p)} = \frac{\varepsilon}{4\pi e c_0(\mu_n + \mu_p)}. \tag{5}$$

It can be seen that the scaling of the space coordinate is the Debye length L_D, while the time scaling is the dielectric relaxation τ_D. Another assumption, usually accepted is the validity of the general Einstein-Nernst relation:

$$\frac{kT}{eZ_i}\mu_i = D_i; \qquad i = n, p. \tag{6}$$

Finally, we can obtain the following system of first order nonlinear partial differential equations:

$$\frac{\partial n}{\partial x} = N - Z_n n E, \tag{7}$$

$$\frac{\partial N}{\partial x} = \left(\frac{1+\pi_m}{\pi_m}\right)\left(\frac{Z_n}{Z_n+Z_p}\right)\frac{\partial n}{\partial t}, \tag{8}$$

$$\frac{\partial p}{\partial x} = R + Z_p p E, \tag{9}$$

$$\frac{\partial R}{\partial x} = (1+\pi_m)\left(\frac{Z_p}{Z_n+Z_p}\right)\frac{\partial p}{\partial t}, \tag{10}$$

$$\frac{\partial E}{\partial x} = \frac{p-n}{Z_n+Z_p}, \tag{11}$$

$$\frac{\partial Y}{\partial x} = -E. \tag{12}$$

Here $\pi_m = (\mu_n/\mu_p)$ is the ratio of the mobility of the negative to the positive ions. The variables $R(x,t)$ and $N(x,t)$ are the positive and negative ion fluxes defined by (9) and (7) correspondingly, while $Y(x,t)$ is the electric potential defined by (12). Equations (8) and (10) are the transport equations for the negative and positive ion charges correspondingly. Equation (11) is the Poisson equation.

The dimensionless total current can be defined from (2), (2) and (3) as follows:

$$I = \frac{R}{1+\pi_m} - \frac{N}{1+\pi_m^{-1}} + \frac{\partial E}{\partial t}. \tag{13}$$

We assume that the electric potential is switched-on infinitely fast at $t = 0$. Then we have the following initial conditions for the above system of equations:

$$n(x, t=0) = 1; \qquad p(x, t=0) = 1; \qquad Y(x, t=0) = \frac{Bx}{M}. \tag{14}$$

where $B = eY_0/kT$ is the dimensionless electric potential. Immediately after the electric field is switched-on, and before the ions have been rearranged by migration and diffusion, the potential Y has a linear dependence over x as in a dielectric.

Four boundary condition express the fact that the electrodes are blocking and hence the ion fluxes N and R are zero at both boundaries $x = -M$ and $x = M$:

$$N(x=-M,t) = N(x=M,t) = R(x=-M,t) = R(x=M,t) = 0. \tag{15}$$

Two other boundary conditions show that the external electric potential is kept constant in time at the two boundaries:

$$Y(x=-M,t) = -B; \quad Y(x=M,t) = B. \tag{16}$$

3. NUMERICAL ALGORITHM

We shall use an algorithm [8], based on the idea to approximate the nonlinear terms in equations (7) and (9) by shifting one of the variables with one time-step.

For an arbitrary function $f(x,t)$ we accept the following rule of discretizing the time and the space:

$$f(x,t) = f_i^k(x_i, t_k). \tag{17}$$

If we denote the space-step with h and the time-step with τ the algorithm can be presented in a general form as follows:

$$\frac{E_{i+1}^k - E_i^k}{h} = \frac{p_i^{k-1} - n_i^{k-1}}{Z_n + Z_p}, \tag{18}$$

$$\frac{Y_{i+1}^k - Y_i^k}{h} = -E_i^k, \tag{19}$$

$$\frac{N_{i+1}^k - N_i^k}{h} = \left(\frac{Z_n}{Z_n + Z_p}\right)(1 + \pi_m^{-1})\left(\frac{n_i^k - n_i^{k-1}}{\tau}\right), \tag{20}$$

$$\frac{n_{i+1}^k - n_i^k}{h} = N_i^k - Z_n n_i^k E_i^k, \tag{21}$$

$$\frac{R_{i+1}^k - R_i^k}{h} = \left(\frac{Z_p}{Z_n + Z_p}\right)(1 + \pi_m)\left(\frac{p_i^k - p_i^{k-1}}{\tau}\right), \tag{22}$$

$$\frac{p_{i+1}^k - p_i^k}{h} = R_i^k + Z_p p_i^k E_i^k. \tag{23}$$

4. ELECTROSTATIC FORCES

Having evaluated the dynamics of the ion charge densities and of the electric field in the cell, we can evaluate also the dynamics of the transient electrostatic forces acting upon the electrodes. To find the mechanical force a general energy approach is useful since it automatically takes into account all hidden factors. The total potential energy $U(t)$ of the electrostatic field $E(t)$ created by all the charges in a volume V, is given by a volume integral [9]:

$$U(t) = \frac{1}{8\pi}\int\limits_V E^2(t)\mathrm{d}V. \tag{24}$$

In the geometry of the concerned cell, all variables are expressed per unit electrode surface, and the surface energy $W(t)$ is given by one dimensional integral as follows:

$$W(t) = \frac{1}{8\pi}\int\limits_{-M}^{M} E^2(x,t)\mathrm{d}x. \tag{25}$$

Small variances of the energy due to a change of the slab thickness, caused by a displacement h of a mobile electrode at $x = -M$, will be given as follows:

$$W(h,t) = \frac{1}{8\pi} \int\limits_{-M\pm h}^{M} E^2(x,t)\mathrm{d}x. \tag{26}$$

Now the electrostatic force acting upon unit surface of the mobile electrode will be given by differentiation of the energy relative to the general coordinate h

$$F(h,t) = \frac{1}{8\pi}\frac{\partial}{\partial h} \int\limits_{-M\pm h}^{M} E^2(x,t)\mathrm{d}x = -\frac{1}{8\pi}E^2(\pm h,t). \tag{27}$$

As the displacement h is a small deviation from the cell thickness we can express the electrostatic force at the electrode as follows:

$$F(h=0,t) = F(x=-M,t) = -\frac{1}{8\pi}E^2(x=-M,t). \tag{28}$$

The formula (19) is valid for the electrostatic force of a dielectric slab [10], where the electric field is homogeneous in the slab and its dynamics is defined solely by the time dependence of the external electric source and the corresponding electric circuits. However, in the case of an electrolytic slab the electric field is nonuniform in the solution, normally to the electrodes, and its time dependence is defined by the dynamics of the ion charge densities responding to the external voltage, as seen from equations (9), (10) and boundary conditions (14).

5. RESULTS AND DISCUSSION

Our main goal is to analyze the time dependencies of the electrostatic force and the other variables considered, but the space distributions can also be instructive. The electric field space distribution, along the coordinate X, is shown in Fig. 2 for equal and different ion mobility, at a fixed moment. The continuous line curve is symmetrical to $x = 0$ and corresponds to the case when the two types of ions have equal mobility, i.e., $\pi_m = 1$. The dashed line corresponds to the case when the negative ions are twice faster than the positive ions, i.e., $\pi_m = 2$ and asymmetry can be observed, the field being stronger in the vicinity of the electrode where the negative charges are attracted. Evidently the field strength is maximal at the electrodes and near zero in the bulk of the solution. Thus, the electrostatic forces are maximal at the electrodes. Obviously if the electrodes of the electrolytic cell are not isolated, the ion charges will not be blocked at the electrodes and the electric field will be smaller, hence the electrostatic force will be small.

We shall analyze the transient processes in the cell in response to a meander-shaped voltage, as shown with thicker lines in Fig. 3.

In fact it is the minimum pulse length of only one cycle. The changes of the voltage from one value to another are assumed infinitely fast in order to analyze the transient response of the system. Four transient periods can be distinguished, denoted with numbers as follows:

1—polarization of the electrodes, forced by a voltage B,

2—depolarization to a neutral charge density, forced by reversed potential $-2B$,

3—polarization with opposite charge, forced by the reversed potential,

4—depolarization due to diffusion of the ion charges back to equilibrium.

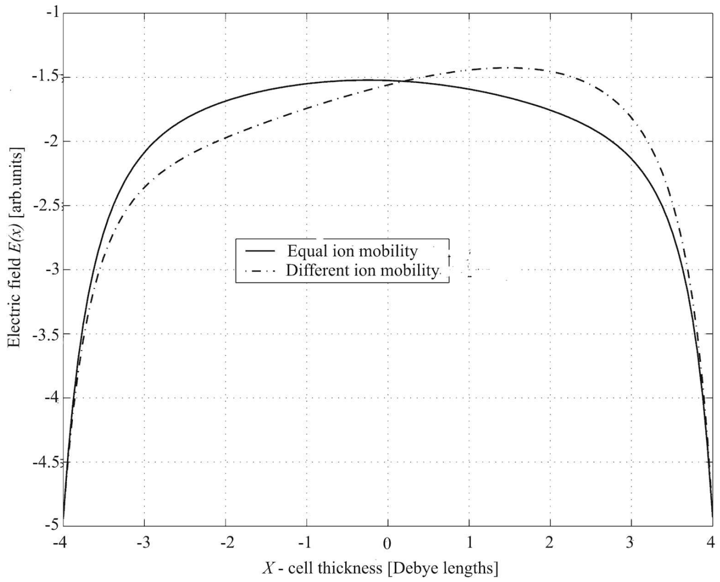
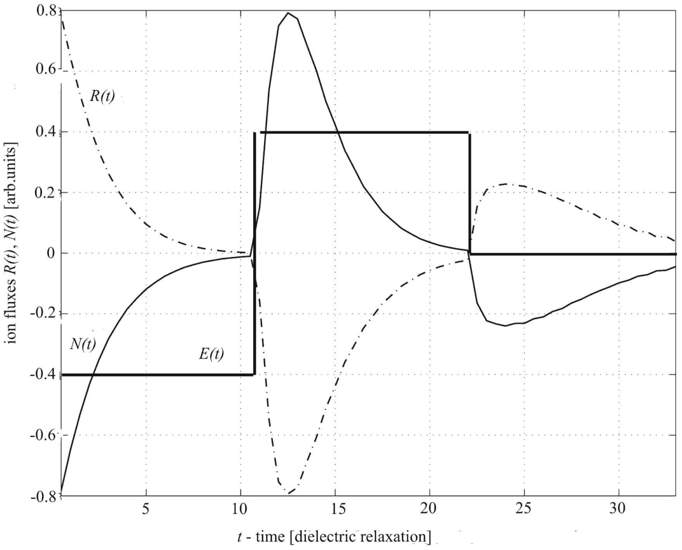


Fig. 2. Electric field distribution, normal to the electrodes

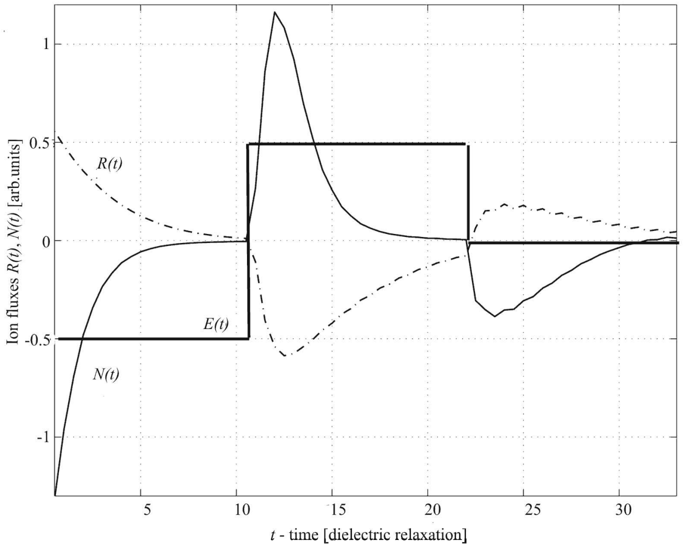
The time dependence of the averaged over the cell length, positive and negative ion currents $R(t)$, $N(t)$, in the four time intervals, are shown in Fig. 3a for a symmetrical electrolyte when $Z_n = Z_p = 1$ and $\pi_m = 1$ while the same curves for the case when $\pi_m = 2$ are shown in Fig. 3b. The meander-shaped external electric field $E(t)$ is shown with thicker lines. It can be seen that the current $N(t)$ of the twice faster negative ions has higher amplitude and shorter relaxation time in comparison with $R(t)$.

The transient displacement current is shown in Fig. 4.

It can be seen that the contribution of the displacement current when the electric field varies due to ion migration can be neglected. The displacement current is dominant only when the external electric field changes very fast.



(*a*)



(*b*)

Fig. 3. Time dependence of the space-averaged positive $R(t)$ and negative $N(t)$ ion fluxes: (*a*) symmetrical electrolyte $Z_n = Z_p = \pi_m = 1$; (*b*) different ion mobility $\pi_m = 2$

The total current comprising the contributions from the ion charge currents and the displacement current, see equation (13), is shown in Fig. 5. The four transient periods are denoted with numbers 1, 2, 3 and 4 as explained above.

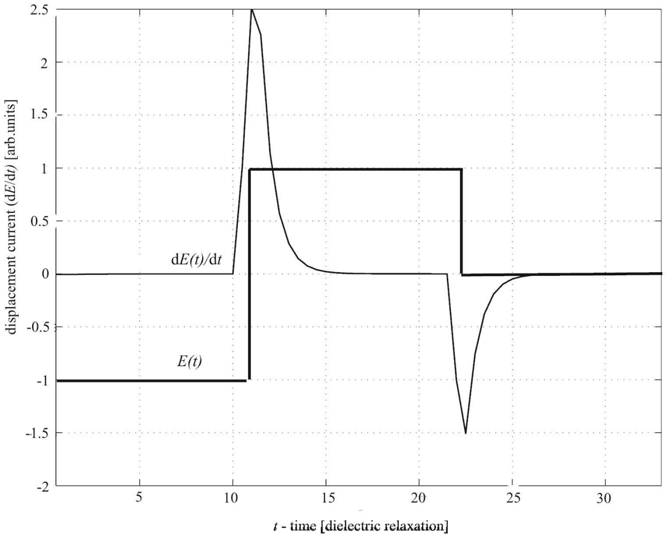


Fig. 4. Time dependence of the displacement current $\mathrm{d}E(t)/\mathrm{d}t$

The time dependence of the electrostatic force $F(t)$ caused by the meander-shaped voltage (presented with thicker line) is shown in Fig. 6 for three different cell thickness values $M = 2, 4$ and 6. The electrostatic force does not change its sign, so it is unidirectional.

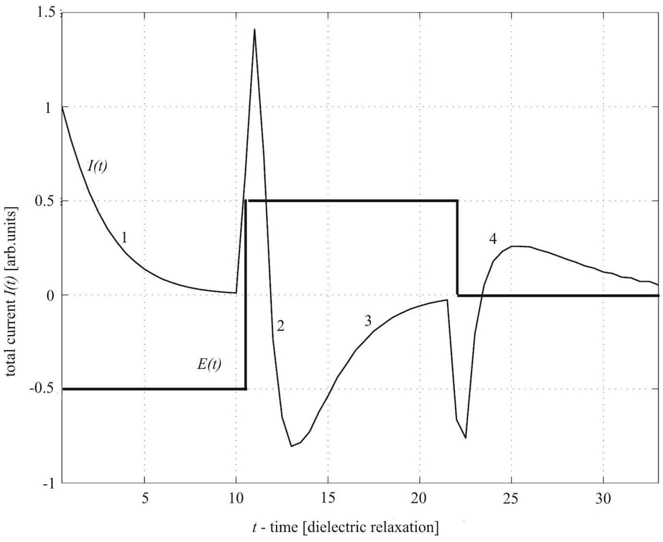


Fig. 5. Time dependence of the total current $I(t)$

If the external electric field is kept constant the electrostatic force is also reaching a constant equilibrium value, as seen in the upper parts of the curves 1 for thinner cells ($M = 2$ and $M = 4$). For thicker cells ($M = 6$), this equilibrium is achieved more slowly. The force is acting as long as the energy of the electric field is not zero, as seen from equation (28). It can be noticed that the transient processes are fastest for the thinnest cell $M = 2$, but the depolarization 2 is deeper for the thicker cell $M = 6$. In the general case the fastest process is the field-forced depolarization 2, while the diffusion depolarization 4 is the slowest. The polarization slopes 1 and 3 are almost identical.

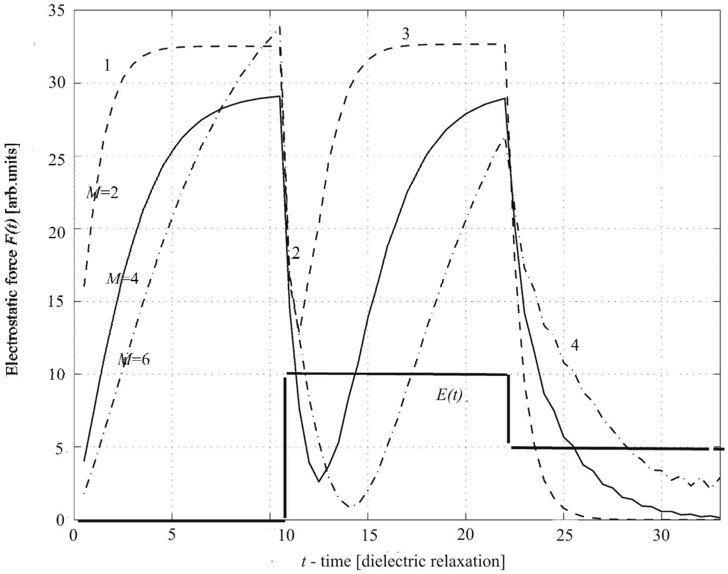


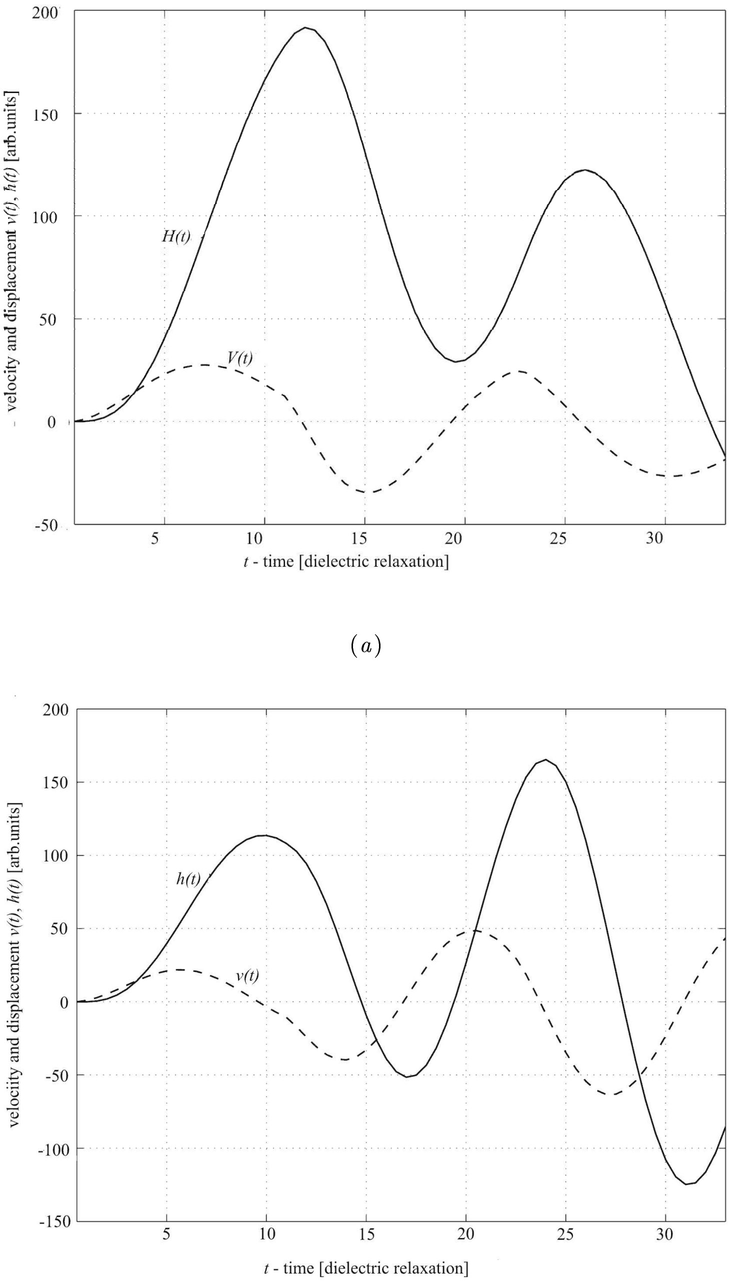
Fig. 6. Time dependence of the electrostatic force $F(t)$ for different cell thickness: $M = 2$, $M = 4$ and $M = 6$

Finally we can evaluate the dynamics of the displacement of the mobile electrode $h(t)$, driven by the electrostatic force $F(t)$. For this reason, we have to solve numerically the equations of forced oscillations, as follows:

$$\frac{\mathrm{d}v(t)}{\mathrm{d}t} = \frac{F(t)}{m} - \frac{k}{m}h(t) - \frac{\eta}{m}v(t), \tag{29}$$

$$v(t) = \frac{\mathrm{d}h(t)}{\mathrm{d}t}. \tag{30}$$

Here $v(t)$ is the velocity of the diaphragm, m is its mass per unit area, k is elastic constant and η is a friction coefficient. Equations (20) are easily digitized and using the results for the driving electrostatic force we can evaluate numerically the displacement $h(t)$ and the velocity $v(t)$. The result is shown in Fig. 7a for the case



(a)

(b)

Fig. 7. Time dependence of the velocity and displacement of the mobile electrode: (a) dominant friction losses; (b) dominant elastic forces

of dominant friction losses and in Fig. 7*b* for the case of dominant elastic forces.

In conclusion we can summarize, that a numerical analysis is carried to evaluate the electrostatic forces when a meander-shaped voltage is applied to an electrolytic cell with blocking electrodes. The algorithm can be easily modified in a future work to simulate the displacements of the mobile electrode when a sinusoidal voltage is applied. Further on a Fast Fourier Transform can by used to obtain the frequency spectra of the electroacoustic signal, which can be compared with experimental results [4].

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Received December 2004