Stabilization of Conducting Pores in BLM by Electric Current

V. F. PASTUSHENKO and YU. A. CHIZMADZHEV

Institute of Electrochemistry, Academy of Sciences of the USSR, Leninsky pr. 31, 117071 Moscow V-71, USSR

Abstract. The free energy of a membrane system as a function of the pore size has been calculated. It is shown that consideration of finite conductivity of a pore leads to an increase in the height of the energy barrier and to an increase in the calculated lifetime of the membrane in the field. It is also shown that there exists a critical value of parameter $s = \sigma\delta/\gamma$ below which, in some intermediate voltage region, splitting of the energy barrier occurs. The condition, which is practically always valid, of the smallness of the input resistance compared with the pore resistance with minimum sizes of the pore is sufficient for the existence of this effect. The relation between the heights of the barriers depends upon parameter s and upon voltage, in which case, with increasing s and ω, the height of the second barrier decreases more rapidly than that of the first barrier. A curve $s(\omega)$ is plotted which limits the region of s and ω values where the splitting effect takes place. It is shown that this curve has a cusp singularity. This feature of the curve $s(\omega)$ is of the same degree of generality as the energy barrier splitting effect itself.

Key words: Electrical breakdown — Conducting pores — BLM stability

Introduction

Various approaches to the study of stability of bimolecular membranes are based, as a rule, on the idea about structural defects of membranes. Such defects are usually represented as through hydrophilic pores. The dependence of free energy of a system on the size of a defect, calculated differently in various concrete models (Chizmadzhev et al. 1979; Derjagin and Gutop 1962; Kashchiev and Exerova 1980; de Vries 1958), is of great importance in kinetic stability theory (Zeldovich 1942; Lifshits and Pitayevsky 1979). In the work of Pastushenko et al. (1979a) devoted to the theory of electrical breakdown of bilayer lipid membranes (BLM) the free energy was calculated under the assumption of low conductance of defects. The obtained dependence of free energy on the defect radius was described by a curve with a maximum, in which case the maximum point corresponded to the critical size of a defect. Generally speaking, with sufficiently large radii of a pore its conductance cannot be considered small. Consideration of this circumstance leads, as will be shown below, to a considerable and sometimes essential change in the free energy of a system depending upon the defect radius. In particular, the appearance of a metastable pore becomes possible (at corresponding values of surface and linear tension), which corresponds to an intermediate minimum on the free energy curve.

Formulation of the Problem

Consider a membrane on both sides of which there is a symmetric electrolyte solution (Fig. 1). A structural defect will be represented as a cylindrical through

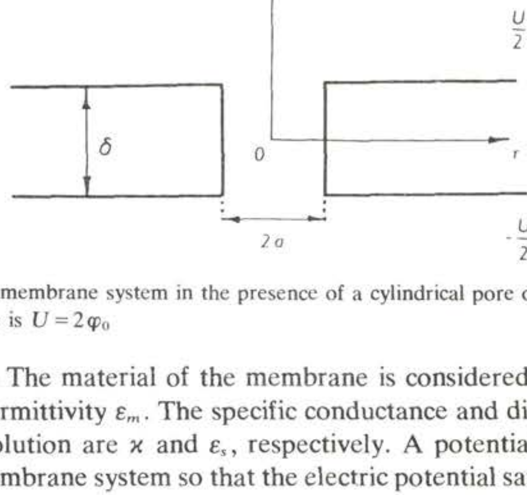

Fig. 1. Diagram of a membrane system in the presence of a cylindrical pore of radius a. The voltage across the membrane is $U = 2\varphi_0$

pore of radius a. The material of the membrane is considered to be an insulator with dielectric permittivity ε_m. The specific conductance and dielectric constant of the electrolyte solution are $\varkappa$ and ε_s, respectively. A potential difference $2\varphi_0$ is applied to the membrane system so that the electric potential satisfies the following conditions:

$$\varphi(r,z) \to \varphi_0, \qquad (r^2+z^2 \to \infty,\ z > \delta/2);$$
$$\varphi(r,z) \to -\varphi_0, \qquad (r^2+z^2 \to \infty,\ z < -\delta/2)\,. \tag{1}$$

Here r and z are cylindrical coordinates (Fig. 1). The symmetry of the system along with conditions (1) also requires the following condition to be fulfilled:

$$\varphi(r,0) = 0\,. \tag{2}$$

This enables us to confine consideration to an electric field in the region $z > 0$. We shall suppose that the electrolyte concentration is sufficiently high so that the thickness of the diffuse layer (the Debye length) is small compared with the membrane thickness. Then in the region $z > \delta/2$ the potential distribution is described by the Laplace equation

$$\Delta\varphi = 0\,. \tag{3}$$

In passing over into the pore the situation is complicated by a number of circumstances: the presence of image forces and their dependence on the radial coordinate, the presence of mouth regions in the pore which are affected by the dependence of image forces on coordinate z and, finally, the presence of a strong electric field which leads to a nonlinear dependence of the pore conductance on the potential difference across the mouth regions. For this reason the problem of an electric field within a pore deserves special consideration. In the present paper the following approach will be used. We assume that the mouth regions of the pore are equipotential, i.e.

$$\varphi\left(r, \frac{\delta}{2}\right) = \varphi_a = \text{const}, \qquad (r \leqslant a)\,. \tag{4}$$

We also assume that the standard chemical potential of ions within the pore is independent of coordinates r and z. Then it can be shown (Markin and Chizmadzhev 1974) that in the constant field approximation the electrolyte within the pore should be regarded as an ohmic conductor with resistance

$$R_p = \frac{\delta}{\pi \varkappa a^2} \exp\left(\frac{\mu^0}{kT}\right) \tag{5}$$

Here μ^0 is the standard chemical potential of ions within the pore and kT is the characteristic thermal energy of a particle. For estimating the μ^0, we shall make use of the result of the work by Parsegian (1969):

$$\mu^0 = \frac{e^2}{a\,\varepsilon_m} P\left(\frac{\varepsilon_m}{\varepsilon_s}\right). \tag{6}$$

Here $P(\varepsilon_m/\varepsilon_s)$ is the familiar function (Parsegian 1969). Let us define, at last, the boundary conditions for Eq. (3). In addition to conditions (1) and (4), one should consider as the boundary condition the absence of the normal current component on the membrane surface:

$$\frac{\partial \varphi}{\partial z} = 0 \qquad \left(r > a,\, z = \frac{\delta}{2}\right). \tag{7}$$

Within the nonconducting material of the membrane the potential distribution can be found by solving Eq. (3) at the given value of the potential at the boundary of the region. To this end use is made of condition (2) and of the solution of the problem determined by Eq. (3) with additional conditions (1), (4) and (7). Our task is to calculate the free energy of the system as a function of the pore radius.

Results

We write the free energy of the system as (Pastushenko et al. 1979a):

$$F = 2\pi\gamma a - \pi\sigma a^2 + F_{el} \tag{8}$$

Here σ and γ are the coefficients of surface and linear tension, respectively, and F_{el} is the part of free energy, due to the electric field. First calculate the change in free energy, resulting from the application of a field of infinitesimal deformations, on the medium, described by vector $\boldsymbol{l}$. This change has the following form

$$dF_{el} = \frac{1}{2}\int \boldsymbol{l}\cdot\left\{E^2 \operatorname{grad}\varepsilon - \operatorname{grad}\left(E^2\varrho\frac{\partial\varepsilon}{\partial\varrho}\right)\right\}dV\,,$$

$$(dV = 2\pi r dr dz)\,. \tag{9}$$

Here E is the electric field strength, ϱ the density of the medium, and ε is the dielectric constant of the medium as a function of space coordinates. The partial derivative $\frac{\partial\varepsilon}{\partial\varrho}$ is calculated at constant temperature T. If the compressibility of dielectrics in neglected, then, as can be shown, the second term in Eq. (9) becomes zero. The field of deformations will be chosen so that it corresponds to the radial displacement of the cylindrical wall of the pore by a value da. Then the required change in free energy, as Eq. (9) suggests, has the form

$$dF_{el} = -\pi a\delta(\varepsilon_s - \varepsilon_m)E_a^2 da\,. \tag{10}$$

Here E_a is the electric field strength on the wall of the pore

$$E_a = \frac{2\varphi_a}{\delta}\,. \tag{11}$$

The potential φ_a occurring in this expression depends on the current I through the pore as follows:

$$\varphi_a = \frac{1}{2}IR_p\,. \tag{12}$$

The value of the current can be found using the results of the work of Newman (1966), where the problem (3), (1), (4), (7) is solved

$$I = (\varphi_0 - \varphi_a)4\varkappa a\,. \tag{13}$$

Eqs. (12) and (13) yield the following expression for the required potential φ_a:

$$\varphi_a = \frac{\varphi_0}{1+\lambda} \tag{14}$$

Here λ represents the ratio of the input resistance $R_i = \frac{1}{2\varkappa a}$ to the resistance of the pore R_p:

$$\lambda = \frac{\pi a}{2\delta} \exp\left(-\frac{\mu^0}{kT}\right). \tag{15}$$

Integrating Eq. (10), we obtain the final expression for the free energy of the system, taking into account the flow of electric current:

$$F = 2\pi\gamma a - \pi\sigma a^2 - \frac{4\pi}{\delta}(\varepsilon_s - \varepsilon_m)\varphi_0^2 \int_0^a \frac{a\,\mathrm{d}a}{(1+\lambda)^2}. \tag{16}$$

Discussion

As is evident from the derivation, the electric term in the free energy (Eq. (16)) describes the work performed by the electric field with varying radius of the pore. It appears from Eq. (10) that this work can be interpreted directly as a result of the effect of a force applied radially to the cylindrical wall of the pore. As is known, a force at the interface between two dielectrics in the presence of an electric field is directed towards the dielectric with the smaller dielectric constant, calculations showing that the work of this force is identical with expression (10).

It is easy to see that at $\lambda = 0$, Eq. (16) is the same as the result of the work by Pastushenko et al. (1979a) in which the influence of the pore conductance was ignored. It is clear that for $\lambda > 0$ the free energy of the system is higher than for $\lambda = 0$. This means that neglect of the pore conductance leads to an underestimated value of the energy barrier surmounted by the pore in the course of evolution.

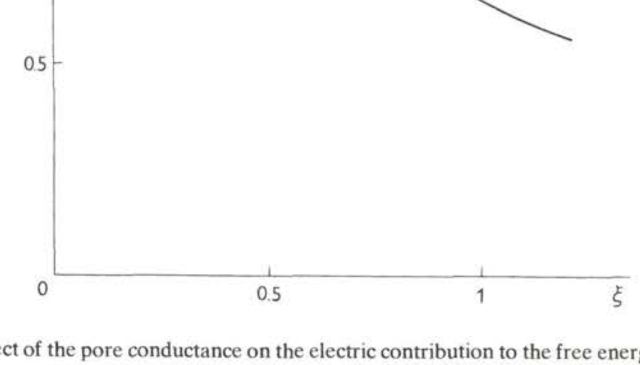

Fig. 2. The effect of the pore conductance on the electric contribution to the free energy of the system.

Correspondingly, the lifetime of the membrane turn out to be underestimated. For this reason it seems to be very important to find the region of parameters where the influence of conductance has to be taken into account. To this end, consider the electric contribution to the free energy as a function of two variables: $F_{el} = F_{el}(a, \lambda)$ and write the relation

$$f(\xi) = \frac{F_{el}(a, \lambda)}{F_{el}(a, 0)}. \tag{17}$$

Here $\xi = \frac{a}{\delta}$ is the dimensionless radius of the pore. The quantity f is a convenient characteristic of discrepancy between the two versions of the theory. Fig. 2 shows the dependence $f(\xi)$ at $\varepsilon_m = 2$, $kT = 4 \times 10^{-21}$ J. As was expected earlier (Pastushenko et al. 1979a), at sufficiently small sizes of the pore, practically when $\xi < 0.5$, it is safe to ignore the effect of conductance on the pore energy. However, the value of the critical radius corresponding to the maximum energy is also a function of parameters γ and σ. Therefore, the final solution to the problem of the role of pore conductance can be found by analyzing the behaviour of the critical radius which is determined from the following equation for ξ:

$$1 - s\xi = \omega g(\xi), \tag{18}$$

where

$$g(\xi) = \frac{\xi}{[1 + \lambda(\xi)]^2};$$

$$s = \frac{\sigma\delta}{\gamma}, \qquad \omega = \frac{U^2(\varepsilon_s - \varepsilon_m)}{2\gamma}, \qquad U \equiv 2\varphi_0.$$

At the above-mentioned values of ε_m and kT we have $\frac{e^2}{\varepsilon_m kT} P\left(\frac{\varepsilon_m}{\varepsilon_s}\right) \frac{1}{\delta} \approx 1$ and, hence,

$$\lambda(\xi) \approx \frac{\pi}{2} \xi \exp\left(-\frac{1}{\xi}\right). \tag{19}$$

It will be shown that at sufficiently small values of s Eq. (18) has three roots, which corresponds to the splitting of the energy barrier. The possibility of occurence of this effect was discussed previously in the work of Abidor et al. (1979). Naturally, in the theory of electric breakdown, the appearance of an additional energy barrier involves the need of taking into account an additional stage of evolution of defects (Abidor et al. 1979; Pastushenko et al. 1979b; Arakelyan 1980). Let us consider in more detail at which values of s and ω there occurs barrier splitting which arises for the first time when the condition, additional to Eq. (18), is fulfilled:

$$\frac{\partial^2 F}{\partial \xi^2} = 0 \tag{20}$$

Differentiating Eq. (18) with respect to ξ, we derive an additional equation for determining parameters s and ω:

$$s=-\omega\frac{dg}{d\xi}. \tag{21}$$

Functions

$$\omega(\xi)=\frac{1}{g(\xi)-\xi\dfrac{dg}{d\xi}}, \tag{22}$$

$$s=\left[\xi-\frac{d\xi}{d\ln g(\xi)}\right]^{-1} \tag{23}$$

are the solution of the system of Eqs. (18) and (21). Thus, barrier splitting occurs on the curve $s(\omega)$ given parametrically by equations (22)—(23). Since $s>0$, it follows from Eq. (21) that the range of variation in parameter ξ is determined from the condition

$$\frac{dg}{d\xi}<0. \tag{24}$$

We thus obtain

$$\xi>\xi_1>0, \tag{25}$$

where ξ_1 is the maximum point $g(\xi)$:

$$\left.\frac{dg}{d\xi}\right|_{\xi=\xi_1}=0. \tag{26}$$

Differentiating Eq. (22), we have

$$\frac{d\omega}{d\xi}=\omega^2\xi\frac{d^2g}{d\xi^2} \tag{27}$$

It thus appears that parameter $\omega(\xi)$ passes through a minimum at a point ξ_2 which is the point of inflection of the function $g(\xi)$. Similarly, from the expression

$$\frac{ds}{d\xi}=-g\omega^2\frac{d^2g}{d\xi^2} \tag{28}$$

we deduce that at the point ξ_2 parameter s reaches its maximum value. Combining Eqs. (27) and (28) we get

$$\frac{ds}{d\omega}=-\frac{g}{\xi}. \tag{29}$$

This signifies that over the whole curve $s(\omega)$

$$\frac{ds}{d\omega}<0 . \tag{30}$$

Furthermore, since the right side of Eq. (29) has no singularities at the point ξ_2, it is clear that the curve $s(\omega)$ at the minimum value of $\omega=\omega_*$ and the maximum value of $s=s_*$ is formed by merging two curves. Thus, on the curve $s(\omega)$ there appears a singularity of the cusp type. Fig. 3 shows a curve of this type plotted from

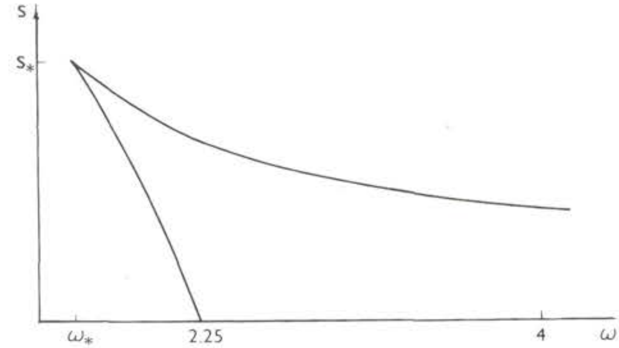

Fig. 3. The boundary between the regions with one and two energy barriers. The values of the parameters $s_*=0.33$ and $\omega_*=1.666$ correspond to the cusp singularity of the curve $s(\omega)$.

Eqs. (21) and (22). In effect, the plotted curve limits the region in which the influence of the pore conductance is most significant. Clearly, when $s>s_*$ there is only one maximum, the influence of conductance decreasing with increasing s.

Consider the dynamics of the energy profile as a function of voltage for $s<s_*$.

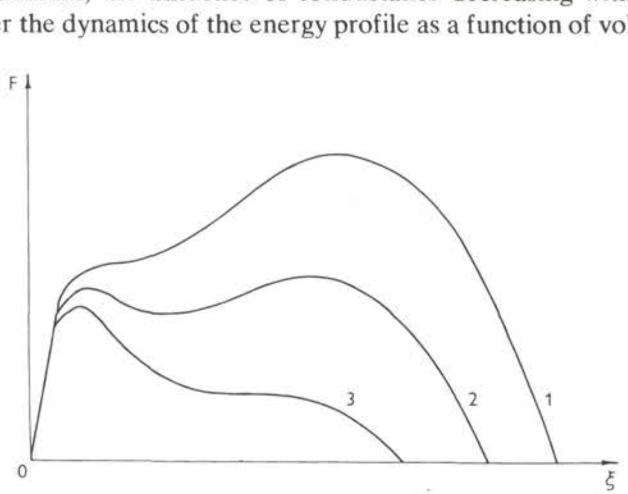

Fig. 4. The free energy of the system against the dimensionless radius of the pore ξ. With increasing number of the curve the voltage across the membrane increases.

Fig. 4 presents three curves plotted at $s = 0.2 < s_* = 0.33$. Curves 1 and 3 were plotted with values of ω such that $s(\omega) = 0.2$. Curve 2 corresponds to the intermediate value of ω. It appears even from this figure, that as the voltage increases the height of the second barrier decreases. It can be shown that this is valid for all $s < s_*$.

It is of interest to consider the relation between the heights of the first and second barrier. Since the height of the second barrier is maximal on the left branch of the curve $s(\omega)$, it is sufficient to consider the relation between the heights on this branch. One can readily see that at $s = s_*$ the height of the second barrier is zero, and with decreasing s the height of the second barrier increases. As $s \rightarrow 0$, this height increases as $1/(2s)$ whereas the height of the first barrier tends to a constant equal to

$$F(\xi_1) = 2\pi\gamma\delta\left[\xi_1 - \omega_* \int_0^{\xi_1} \frac{x\,dx}{[1 + \lambda(x)]^2}\right]. \tag{31}$$

Thus, at sufficiently small values of s the second barrier can be arbitrarily large compared with the first barrier.

It is worth noting that when $s = s_*$ and $\omega = \omega_*$ the curvature of the barrier at the maximum point is zero. This example indicates that in the general case it is not enough to describe the barrier by its curvature alone at the maximum point, as was done, for example, by Derjagin and Prokhorov (1980).

We discuss, finally, the question as to what extent the energy barrier splitting effect is an off-model result. As follows from the derivation, the splitting effect results from the occurrence of a maximum of function $g(\xi)$. The nonmonotony of $g(\xi)$ is in turn ensured if at small sizes of the pore $\frac{dg}{d\xi} > 0$, i.e. if the following condition holds:

$$1 + \lambda > 2\xi \frac{d\lambda}{d\xi}. \tag{32}$$

Obviously, this condition will be fulfilled practically always at sufficiently small ξ. In other words, it is required that, with small radii of the pore, parameter λ should be sufficiently small, which seems to be valid irrespective of the assumption of the cylindrical shape of the pore and even of the effect of image forces which prevent ions from penetrating the pore. Thus, the use of Eq. (6), suitable for the case of a long pore filled with pure dielectric, is only corrective in character and does not affect the conclusion about the existence of the splitting effect.

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