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CONDUCTIVITY AND SEMICONDUCTIVE PARAMETERS OF BIOLOGICAL MEMBRANES

There are tunnel nature of transmembrane current and ideas of mechanisms of this current summarized in the article. The calculation of the parameters characterizing conductivity of membranes, in particular, kinetics of electronic transitions, specific conductivity, mobility and the concentration of carriers allows to consider a biological membrane as the equivalent semiconductor. The material of this article is directed, in particular, to a problem of development and research of biotechnical devices on the basis of the natural and synthesized biological membranes.

Keywords: transmembrane current, tunneling, membrane semiconductor, semiconductor parameters

INTRODUCTION

The electron transport mechanism research began from the study of the photoinduced oxidation of cytochromes in the photosynthesizing bacteria of Chromatium, that is the transfer of electrons from cytochrome to the reaction center of chlorophyll. Further low-temperature measurements allowed, firstly, to study temperature dependence of conductivity, and, secondly, to detect electron tunneling. By 1960 Chance and Nishimura [1] have already revealed electron transfer through the respiratory chain at the temperatures below the liquid nitrogen. In 1966 De Vault and Chance [2] investigated temperature dependence of cytochrome oxidase conductivity within the temperature range from 31 to 298 K and found that electron tunneling began at low temperatures (< 65 K), while semiconductive character of temperature dependence prevailed at higher temperatures, that is the Arrenius increase $\exp(-E_a / kT)$. A little later the results of the researches for temperature dependence of conductivity were summarized by Joertner [3] in the form of the succeeding propositions: the measured half oxidation time of the cytochrome is $\tau_{1/2} = 2.3$ ms at temperature 4.5 K; the time $\tau_{1/2}$ is practically constant in the temperature range $4.5 \div 100$ K; and the activation energy of conductivity under these conditions is within $3.5 \cdot 10^{-3}$ eV ; the time $\tau_{1/2}$ decreases from 2.3 ms to 2 μs in the range of (100–300) K; temperature dependence of the time corresponds the activation energy of 0.14 ±0.03 eV in the range of (100–300) K, that is approximately 5.5 *kT* at the temperature of 300 K.

It has become clear [4], that the pure periodic lattice was not a necessary condition for electron transport. There is necessary only sufficiently strong interaction of the carriers, facilitating free electron states collectivization.

Electron transport has extensively became the research focus studying the chemical reactions in solutions and then in heterogeneous mediums, and in particular, in biological membranes, where there are well-structured in space and temporally arranged donor-acceptor pairs.

The natural and artificial biological membranes have found their application for construction of measuring systems (biosensors) in recent times. They for example, are used for detection of the extracellular signals [5, 6] from the electrogenically reactive cancer cells (HL-1) and the embryonic kidney (HEK293) cells by means of direct electrolythic contact with the floating gates of the complementary pair of field transistors [5]. The subminiaturized diamond transistors have been used [6] for measurement of cells ion-exchange by means of direct electrolytic contact. It is known [7], that there are electron transport chains in the membranes of some electrochemically active bacteria classified as *Exoelectrogens*, which are alternative to the main (respiratory) chain and capable of transferring electrons to any external acceptor, for example, to metals.

The property can be used for anticorrosion protection.The interest in neuroprosthetics [8] has evolved on basis of William Shockley's assumption of semiconductor properties of nervous fibers.

STARTING POSITIONS

The Foerster' studies [9] of excitation energy migration on frequency components of fluorescence spectra by means of dipole-dipole interactions were the point of departure for electron transfer analysis. A little later Dexter [10] studied tunneling electrons transfer for strong orbital overlap at the distance between the donor and acceptor not more than 10–15 Å.

The rate constant for a bimolecular reaction in a solution (reactants encounter frequency), which initially was obtained in classical description by statistical mechanic methods and was written as a common expression of the form

$$K = k(r) A\sigma^2 \exp\left(-\Delta G^* / RT\right),$$

where $k(r)$ — the mean probability of single electron transfer within donor-acceptor pair, which is exponentially dependent on the distance r at long distances and is close to one at small distances; $A\sigma^2$ — the factor determining collision frequency; ΔG^* — the free energy of the reaction; furthermore,

$$\Delta G^* = \left(\lambda/4\right)\left[1+\left(\Delta G_{\text{ET}}/\lambda\right)\right]^2$$

(λ — the reorganization energy; ΔG_{ET} — the transfer driving force). Note, that the standard free energy value ΔG^0 is usually known for reactions in a solution, but is much less known for membrane donor-acceptor pairs.

Initially the quantum-mechanical description of electron transfer in a homogeneous medium (reagents plus a solvent) has been written as [11]

$$K = \frac{2\pi}{\hbar} H_{\text{AB}}^2 (\text{FC}),$$

where (FC) — the factor determined by the adiabatic Franck—Condon principle of constancy of the positions of the interacting nuclei, that is the sum of products of overlap integrals of the vibrational and solvational wavefunctions of the reactants with those of the resultants; H_{AB} — is a matrix element of the connection between electron states of the reactants and the resultants.

Later, with the purpose of semiclassical characterization of electron exchange in a reversible reaction in the theory of Marcus [12] the basic equation for the non-adiabatic electron transfer was obtained

$$k_{\text{ET}} = \frac{2\pi}{\hbar} \cdot \frac{\left|V_{if}\right|^2}{\sqrt{4\pi\lambda k_B T}} \exp\left[-\frac{\left(\lambda+\Delta G\right)^2}{4\lambda k_B T}\right].$$

The equation appears as the quantum-mechanical analog (counterpart) to the Arrhenius equation. The preexponential factor in the equation has dimensions of $\left[\text{s}^{-1}\right]$ and means the electron transitions number per second that is an electric current in a donor-acceptor pair of carrying agents. Therefore, the equation is an analog to current voltage characteristic of transition in relation to one-directional electron transfer. The velocity of electron transfer is determined by the sum of the reorganization energy λ that is the potential energy characterizing electronic carrier configuration variability in a transfer act, and by the change of the Gibbs free energy ΔG considered as a thermodynamic component of an electron transfer moving force. The kinetic component of energy of transfer is determined by exchange interaction (exchange coupling) between electron and oscillation of the atoms of the hypothetical lattice (of a protein). The matrix element $\left|V_{if}\right|$ determines the electron energy-level difference in the initial (i) state (DA) and in the final (f) state (D^+A^-). The Marcus equation during the last decades has been used in miscellaneous applications regarding electron transfer [13].

The semiclassical Gaussian approximation of the electron transfer probability for the locally organized donor-acceptor pair in a membrane, which fits to the process for a quite high temperature, is defined by the formula:

$$W_{\text{sc}} = \frac{2\pi}{\hbar^2\omega} \frac{\left|V_{\text{DA}}(R)\right|^2}{\left[2\pi S\left(2\bar{\nu}+1\right)\right]^{1/2}} \exp\left[-\frac{\left(\frac{\Delta E}{\hbar\omega}-S\right)^2}{2S\left(2\bar{\nu}+1\right)}\right],$$

where $\bar{\nu} = \left[\exp\left(\hbar\omega/\left(k_B T\right)\right)-1\right]^{-1} \cong k_B T/(\hbar\omega)$ (at T= = 300 K); $\Delta E/(\hbar\omega) = P$ (ΔE — conductivity activation energy)); $S = E_{\text{r}}/(\hbar\omega)$ (E_{r} — reorganization energy or else that of recovery of the balanced or, more exactly, initial for the every transfer act configurations of reactants and the resultants; the parameter S

qualifies a binding force; the limitation $S \gg 1$ defines the strong bond; the frequency ω is within the intrinsic frequency band (normal oscillations) of oscillators of the biological environment which quanta $\hbar\omega$ excites transfer.

The potential reorganization energy is a combination of two components. The first of those is defined by change of the reactant elastic link lengths, and the second of those is defined by change of polarization of all groups involved in transfer.

The transmembrane current has a tunneling nature when the distance between active centers of electron carriers is within 5–20Å or still less (as follows for the reactive centers of membrane photosystems). At times, it was considered (comment of V.I. Goldanski) that the tunneling effect has been at the very root of the origin of life.

General properties of the electron transport chain, which are needed for a father evaluation, can be summarized in the form of the following known provisions.

The membrane electron transport chain (the respiratory chain of an animal cell) involves not less than 15 reactions for generation and transport of redox equivalents (H^+, e) and energy production (phosphorylation of ADP). The Grove hydrogen-oxygen cell (W.R. Grove, 1839) can serve as a principal, if crude, analogue of the biological electron transport system. Here, at one electrode (an anode) hydrogen catalytically passes into the components H^+, e; the protons (in the solid polymer electrolyte) and electrons (in the external electric line) transfer to another electrode (a cathode), where the water is generated. The carrier protein chain localized essentially in the membrane body acts as an external electric line conductor in a biological membrane. A single metal atom (Fe, Cu) acts as an electron transfer cofactor but not as an additive agent. The transmembrane electron transfer chain begins from the (H^+, e) source (NAD H_2) and ends with the terminal electron acceptor (½)O_2. The electron transport limiting factors are the inflow of hydrogen and oxygen gases and also the availability of ADP and P_i (inorganic phosphate). The kinetic chain properties which investigation has a long and confusing history are determined by the time of carriers half-oxidation $\tau_{1/2}$ (first-order kinetics). There will be being used data values those are considered as the well adequate (responsible) ones [15]: $\tau_{1/2}$ = 0.51 ms for the unit $a \rightarrow a_3$ and $\tau_{1/2}$ = 0.4 ms for the terminal section

$$a + a_3 \rightarrow (1/2)O_2$$

of the mitochondrial electron transport chain. These values were obtained for the fully reduced anaerobic mitochondria after pulse oxygen supply, namely these ones define just the carrier transient (kinetic) behavior. The value $\tau_{1/2} = 0.4$ ms corresponds to electron transport rate $\ln 2 / \tau_{1/2} \cong 1.7 \cdot 10^3\ \mathrm{s}^{-1}$ and to electric current, per transfer of pair of electrons to oxygen (for quantum forbidding, "one by one"), approximately equal to $5 \cdot 10^{-16}$ A. Note also that a membrane in principle is a current source and not the Maxwell´s applied electromotive force (the galvanic element).

The inequality satisfaction $\xi^2 = \left(\hbar^2 \Big/ \left(2m_e \Delta\varphi_\mathrm{m} d_\mathrm{m}^2\right)\right) \ll 1$, that is the smallness of the quantum volume of activity h in comparison the value of $\sqrt{2m_e \Delta\varphi_\mathrm{m} d_\mathrm{m}^2}$, characterizing the potential (m_e — mass of electron; $\Delta\varphi_\mathrm{m}$ — the transmembrane difference of potentials; d_m — the thickness of membrane). is considered to be quasiclassical approximation condition for the membrane and for character of the transmembrane current [16]. Under the condition of potential linear run in the membrane, that is a mean (average) transmembrane electric field strength $\Delta\varphi_\mathrm{m} / d_\mathrm{m} = 2 \cdot 10^7$ V/m ($\Delta\varphi_\mathrm{m} = 200$ mV; $d_\mathrm{m} = 100$ Å), we get $\xi^2 = 0.0015$, and thus the quasiclassicality condition holds. Under the condition of a potential nonlinear run (the square or trapezoidal potential barrier) the characteristic length $l < d_\mathrm{m}$ near one of the interphase boundaries of "membrane—aqueous environment" or near the both boundaries should be inputed. When substituting the thickness of the membrane, d_m значения характерной длины менее $l = 10$ Å the quasiclassical approximation ceases to be true.

The other condition of membrane quasiclassicality and electron transfer results from the definition of the de Broglie wave length of electron $\lambda = h\left[2m_e\left(E - U(x)\right)\right]^{-1/2}$ (E — total energy of electron; $U(x)$ — potential energy of electron) and is formulated in the form of the inequality [17, 18]:

$$\left|\frac{\mathrm{d}\lambda}{\mathrm{d}x}\right| = \frac{h}{2\sqrt{2m_e}}\left[E - U(x)\right]^{-1/2} \cdot \left|\frac{\mathrm{d}U}{\mathrm{d}x}\right| \ll 1.$$

Providing that $E - U = \Delta\varphi_\mathrm{m}$, in other words excess (kinetic) electron energy corresponds to a potential barrier height, then in case of $l = d_\mathrm{m}$ (the potential linear run) we get

$$\frac{\mathrm{d}\lambda}{\mathrm{d}x} = 0.137$$

and thus the quasiclassical condition holds. However, at $l = 10$ Å ($\mathrm{d}\lambda/\mathrm{d}x = 1.37$) quantum nature of the membrane and electron tunneling are most likely. Accordingly, the magnitude l means a tunneling path in this case. The de Broglie wavelength of electron can be direct enumerate [17] from the expression $\lambda_e = h/\sqrt{3m_e k_B T} = 62$ Å, that is commensurate with the thickness of the membrane. Therefore it is clear, that electron cannot be localized in the donor active center (for example, Fe^{2+}). This status is favorable as in terms of energy exchange with phonons of a hypothetical lattice structure (a protein), as in terms of ease of tunneling.

Electron tunneling has been postulated during investigation of temperature dependence of conductivity of the discontinuous thin metal films on insulating substrates [19]. When decreasing the external bias there were remained electron unidirectional (tunneling) transitions, however when the bias is close to zero but finite these transitions became equally probable in directions $\pm x$ and the conduction current became equal to zero. In this work approximation of zero bias served as proof of tunneling conductance existence. There are also investigated the conduction-related processes (electron transport) in metalloproteins. In this work in particular has been noted, that the tunneling path for the one-step electrontransfer cannot exceed 20 Å.

The transparence of the square barrier for the tunnel electron can be calculated using the formula:

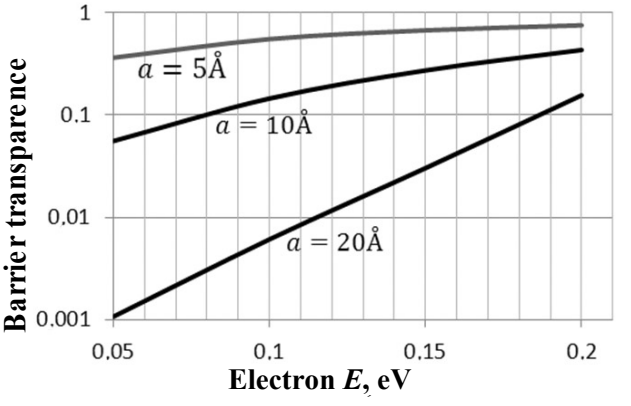
$$D = \left\{1 + \left[\frac{\left(k^2 + \gamma^2\right)\mathrm{sh}\left(a\gamma\right)}{2k\gamma}\right]^2\right\}^{-1},$$

wherein

$$k^2 = 2m_e E_e / \hbar^2; \quad \gamma^2 = 2m_e \left|E_e - U_0\right| / \hbar^2 \left(E_e < U_0\right);$$

a — the width of barri; E_e — electron energy; U_0 — the barrier height defined by transmembrane potential difference, that is. $U_0 = e\Delta\varphi_{\mathrm{m}} = 0.2$ eV. The calculation data is shown in the figure.

In case of the equality of the barrier height and the electron energy $U_0 = E_e = 0.2$ eV if the width of barrier is reduced the transparence approaches one, and



The biological membrane transparence for the tunnel electron at predetermined value of the tunneling path

the transfer process become overbarrier one. However in the case of $E_e = 0.05$ eV the transparence of the thin barrier (5Å) at the expense of tunneling is 500 times as the transparence of the more lengthy one (20Å).

The barrier height $U_0 = 0.2\,\mathrm{eV} \cong 8k_B T$ $(T = 300\,\mathrm{K})$ allows to make an estimate of the scale of the energy obtained by a conduction electron through an energy exchange with phonons of a hypothetical lattice of the donor carrier protein. The barrier transparence at $a = 5$ Å, как это следует из рисунка, равна приблизительно $D = 0.75$. as it follows from Fig., is something like $a = 5$ Å the average electric field intensity equals $E = 4 \cdot 10^8$ V/m, that is 20 times more than the mean for the membrane. Furthermore, the strong electric field presence near the emitter surface makes the barrier acute-angled and facilitates the tunneling.

The membrane tunnel current density can be estimated abiotically as an autoelectronic emission current density. Let us write according to the Fowler—Nordheim's formula:

$$J_{\mathrm{F_g\text{-}N_g}} = \frac{e^3 E^2}{8\pi h e \Delta\varphi} \exp\left[-\frac{8\pi\sqrt{2m_e}\left(e\Delta\varphi\right)^{3/2}}{3heE}\theta\left(y\right)\right],$$

where $e\Delta\varphi$ — the difference of the standard reduction potentials of a donor-acceptor pair of the electron carrier protein; $\theta\left(y\right)$ — the Nordheim tabulated function of the nondimensional variable $y = \left(e / e\Delta\varphi\right)\sqrt{eE / 4\pi\varepsilon\varepsilon_0}$. We use the value $e\Delta\varphi$

for the membrane donor-acceptor pair of the cytochrome $b-c_1$, that is the redox-potential difference $170\,\text{mV}$ and $e\Delta\varphi = 0.17\,\text{eV}$ correspondingly. In case of $\varepsilon = 2 \div 3$, that is, in particular, during the emission to a nonpolar membrane hydrocarbon as well as in case of $\varepsilon = 1$, i.e. during the emission in a vacuum. The calculation at $\theta(y) = 0$ in both cases, gives a high current density value $J_{\text{F}_\text{g}\text{-N}_\text{g}} = 1.46 \cdot 10^{12}\,\text{A} \cdot \text{м}^{-2}$ that is typical for an autoelectronic emission. The current density value should be read as impulse (pulsed; pulsing) one defined by the exchangeable tunneling time. Assume, in the same way as before, the electron transfer time defined by an electron transport chain kinetics is equal to $\tau = 1/\left(1.7 \cdot 10^3\right) = 5.9 \cdot 10^{-4}\,\text{s}$. Here the time τ should be read as the sum of the very short specifically quantum tunneling time $\tau_\text{t} = 10^{-14}\,\text{s}$ and the incommensurably more prolonged relaxation time of the carrier proteins, including donor pumping, acceptor reconstruction (conformational rearrangement) and energy migration in the medium mediating during the transfer. The average in a (the) time τ gives the value of the current density $j = 25\,\text{A} \cdot \text{m}^{-2}$, or, per one respiratory assembly of $5 \cdot 10^{-15}\,\text{m}^2$ something like $10^{-13}\,\text{A}$. Just the same calculation for the barrier width $a = 20\,\text{Å}$ and, correspondingly, for the density of field equal to $E = 10^8\,\text{V/m}$ gives the average value of the tunneling current density near $j = 1\,\text{A} \cdot \text{m}^{-2}$ and something like $10^{-14}\,\text{A}$ per one respiratory assembly.

ESTIMATED RATIOS AND RESULTS OF CALCULATIONS

The formulae obtained in the studies [3, 14] and summarized in the monograph [22] are further used for the calculation of the thermally activated transmembrane tunneling current. Squared electron wavefunction overlap integral in potential wells of a donor and an acceptor is approximated in the form of:

$$I_e^2 = \left|\int \psi_d^*(x)\psi_a(x)\,\text{d}x\right|^2 \approx \exp\left(-\frac{l}{a}\right),$$

where the value a is defined as being $a = \hbar/2\sqrt{2m_e(U-E)}$. The difference $U-E$ defines the potential barrier highness counted from the donor well bottom; it is assumed equal to $U-E = 0.6\,\text{eV}$) in the calculations. The electron transfer constant (frequency) is given by the expression

$$k_\text{ET} = \frac{2\pi}{\hbar} \cdot \frac{\left|V_{if}\right|^2}{\hbar\omega\left[2\pi S\left(2\bar{\nu}+1\right)\right]^{1/2}} \exp\left[-\frac{(P-S)^2}{2S\left(2\bar{\nu}+1\right)}\right],$$

which is equivalent to the Marcus equation, wherein $V_{if} = |E_e| \cdot I_e$ — the matrix element of the electron interaction energy; E_e — the donor electron level denoted [14] as disturbance energy, which is counted from the well bottom and assumed equal to $E_e = 6k_BT$. in the calculations. The parameter $P = \Delta E/(\hbar\omega)$ determines the driving force of transfer that is the difference ΔE of the carrier standard reduction potentials, which is assumed equal to $\Delta E = 0.2\,\text{eV}$. The normal oscillation frequency ω notably of a blend of photons and phonons that Hopfield [14] called polaritons, is assumed equal to $3 \cdot 10^{13}\,\text{s}^{-1}$, that is $\hbar\omega = 0.02\,\text{eV}$ and $P = 10$, accordingly, that corresponds to soft oscillations. The parameter $S = E_\text{r}/\hbar\omega$ defines the reorganization energy $E_\text{r} = (1/2)\Delta^2\hbar\omega$.

Tunneling jump changes the donor and acceptor positions as well as the gravity center position of accepting mode, in other words, the whole of array of the atoms and groups received the transfer energy. When r is the distance between the electron acceptor well center and the center of gravity of the accepting mode till the transfer, then the instantaneous shear of the center of gravity during tunneling transition is determined by the coulombian ratio $\Delta r = e^2(l_1 - r)^2/\left(4\pi\varepsilon\varepsilon_0 l_1^2 r^2 M\omega^2\right)$, where e — the electron charge; l_1 — the donor potential well width; ε — the microscopic dielectric permittivities assumed equal to $\varepsilon = 2$; M, ω — the mass and the frequency of the accepting mode; $M\omega^2$ — the oscillator hardness. The ratio $\Delta = \Delta r/R_0$ (R_0 — the range of zero-point oscillations, $R_0 = 0.01 \div 0.04$ Å) defines the reorganization energy and the electron constraint force in the acceptor; $\Delta \ll 1$ — weak link, the quantum energy $\hbar\omega \approx 0.1 \div 0.2\,\text{eV}$ and hard oscillations; $\Delta \gg 1$ — strong link, the quantum energy $\hbar\omega \approx 0.01 \div 0.02\,\text{eV}$ and soft oscillations consequently. There was chose the reorganization energy equal to $E_r = 0.6\,\text{eV}$. in the calculation. Hence, $S = 30$, that corresponds to the strong link. The equality $U - E = E_r$ corresponds to dissipationless (quasielastic) nature of the reorganization process.

The parameter $\bar{v} = k_B T/(\hbar\omega)$ ($T = 300\,\mathrm{K}$) equals to $\bar{v} = 1.3$; длина туннелирования l the tunneling path $l = 20\,\text{Å}$.

So, we get the value $k_{\mathrm{ET}} = 2.65 \cdot 10^{13}\,\mathrm{s}^{-1}$. of the transition probabilities (transition counts per second). The quantity inverse to the received value, that is the tunneling time for one electron, is $\tau_t = 4 \cdot 10^{-14}\,\mathrm{s}$ and complies with time (Heisenberg) uncertainty. The transmembrane current in the calculation per the pair of respiratory carriers appears to be approximate to $i_1 = 4 \cdot 10^{-6}\,\mathrm{A}$, that is incommensurably large by in comparison with forehand estimation ($10^{-16}\,\mathrm{A}$), describing the kinetic potentials of the terminal respiratory unit. However, the averaging in the same way as it worked during the field emission current estimation under the condition $\tau_t << \tau_1$ gives the value $i_1 \cdot (\tau_t/\tau) = 4 \cdot 10^{-6} \cdot \left(4 \cdot 10^{-14}/5.8 \cdot 10^{-4}\right) \cong 3 \cdot 10^{-16}\,\mathrm{A}$. The value corresponds to the transmembrane current density which approximates to $j = 0.06\,\mathrm{A \cdot m^{-2}}$.

At the average (macroscopic) intensity value of a transmembrane electric field $E = 2 \cdot 10^7\,\mathrm{V \cdot m^{-1}}$ the membrane specific conductivity resulted from expression $j = \sigma E$ (Ohm's law) is equal to $\sigma = 3 \cdot 10^{-9}\,(\Omega \cdot \mathrm{m})^{-1}$. Finally, from the ratio $\sigma = e n_e \mu_e$ at the average mobility value $\mu_e = 10^{-3}\,\mathrm{cm^2/(V \cdot s)}$ (calculated below) the carriers concentration is defined as $n_e = 2 \cdot 10^{11}\,\mathrm{cm^{-3}}$, which corresponds to the upper bound for polymer semiconductors (say for the undoped polyacetylene with conductivity $\sigma = 10^{-8}\,(\Omega \cdot \mathrm{m})^{-1}$). Further calculate the electron mobility. As noted above delocalized electron position in the membrane body promotes, firstly, an energy change with the phonons of hypothetical lattice (of a protein) and, secondly, tunneling transitions (hoppings) through the certain points. The hopping sequence is the Markov process, i.e. an individual events of hoppings don't correlate. It is formally required that the hopping time should be far less than the relaxation time. This condition is easily met for the bulky carrier protein.

It is expected that the delocalized electron acts like a classical diffusing particle. Alternatively this assumption runs into problems. The classical Lorentz radius of the diffusing electron equals to $2.8 \cdot 10^{-15}\,\mathrm{m}$. However, if to use the Stokes—Einstein formula for diffusion coefficient, where the particle radius and the dynamic viscosity are commutatively part of this one, and to take the membrane microviscosity equal to $\eta = 0.1\,\mathrm{Pa \cdot s}\,(1\,\mathrm{poise})$ (experimentally measured for incommensurably more large particles) then the radius appears to be $10^{-19}\,\mathrm{m}$. Therefore it has to take that the Stokes—Einstein formula is impracticable.

Activation hopping probability is defined by the expression $w_e = (\omega/2\pi)\exp\left(-E_a/(k_B T)\right)$, and the one-dimensional (across membrane) diffusion coefficient — by the expression $D = \left(l^2/2\right) \cdot (\omega/2\pi)$; proportionality to frequency means that the hoppings are triggered by the lattice vibration quanta. The using Einstein formula $D = \mu_e k_B T/e$ allows to wright the ratio for the mobility

$$\mu_e = \frac{e}{k_B T} \cdot D = \frac{e l^2}{2\pi\hbar} \cdot \frac{\hbar\omega}{k_B T} \cdot \exp\left(-E_a/k_B T\right).$$

The calculations at the values: $l = 5,\ 20\,\text{Å}$ (the tunneling path); $\omega = 10^{13} \div 10^{14}\,\mathrm{s}^{-1}$ (normal oscillation) and $E_a = 0.2\,\mathrm{eV}$ — give the minimal (at $\omega = 10^{13}\,\mathrm{s}^{-1}$) mobility values $\mu_e = 0.7 \cdot 10^{-4}\,\mathrm{cm^2/(V \cdot s)}$ ($l = 5\,\text{Å}$) and the maximum (at $\omega = 10^{14}\,\mathrm{c}^{-1}$) values $\mu_e = 1.1 \cdot 10^{-2}\,\mathrm{cm^2/(V \cdot s)}$ ($l = 20\,\text{Å}$).

The small mobility value ($\mu \ll 1\,\mathrm{cm^2/(V \cdot s)}$) of current curriers in semiconductors has long been the basis for the concept of the electron hopping from a node to a node. The hopping (μ_h) and tunneling (μ_t) mobilities ratio are discussed at length in the theory of a small radius polaron.

The diffusing particle mean square displacement $\sqrt{\overline{x^2}} = \sqrt{2Dt}$ for the calculated mobility values appears to range within $0.05 \div 0.5\,\text{Å}$. This argue for a multistep tunneling [13] or a series of hoppings on the closely-spaced quantum point contacts.

Frelikh [24] determines the relaxation time or the average time between hoppings by the equation

$$\tau = \frac{1}{2w_{21}} = \frac{\pi}{\omega}\exp\left(H/(k_B T)\right),$$

where H — a barrier height; ω — an electron oscillation frequency near (by) the every equilibrium position on either side (astride) of a barrier;

w_{21} — the transition probability, defined as before by a transition count in a unit of time; moreover, $H \gg k_B T$. The number of electron collisions with their surroundings is that the average time between collisions τ_0 is small in comparison to the average time τ that electron spends near the every equilibrium position namely $\tau_0 \ll \tau$.

Let us now set $n_1(t)$ — the number of particles in position 1(electron donor); $n_2(t)$ — the number of particles in position 2 (electron acceptor); $n_1 w_{12}$ — the number of particles per second, which pass from position 1 to position 2; $n_2 w_{21}$ — the number of particles per second, which pass from position 2 to position 1. Then we can generate, following Frelikh, the set of equations showing electron-transition rates in both directions:

$$\begin{cases} \mathrm{d}n_1/\mathrm{d}t = -n_1 w_{12} + n_2 w_{21}, \\ \mathrm{d}n_2/\mathrm{d}t = -n_2 w_{21} + n_1 w_{12}. \end{cases}$$

Subtracting the first equation from the second one, we get the linear differential equation

$$\mathrm{d}(n_2 - n_1)/\mathrm{d}t = -(w_{12} + w_{21})(n_2 - n_1) + \\ + (w_{12} - w_{21})(n_2 + n_1),$$

to solve this equation at first (at the beginning) we write down the expressions for the both probabilities

$$w_{12} = \frac{\omega_0}{2\pi}\exp\left(-\frac{E_\mathrm{a} - \Delta G}{k_B T}\right), \qquad w_{21} = \frac{\omega_0}{2\pi}\exp\left(\frac{\Delta G}{k_B T}\right),$$

where E_a — activation energy and ΔG — the change of free energy during the transfer; in addition $w_{12} \gg w_{21}$. for an one-direction process. The initial condition is formulated in the form $\Delta n(0) = \\ = [n_2(0)+1] - [n_1(0)-1] = 2,$ that is one activated electron on the donor level and one vacant position (vacancy) on the acceptor level; besides, in virtue of the Markov character of the process the equality $n_2(0) = n_1(0)$ is fulfilled for any number of transfer acts previous to the act under study.

The solution is written notationally $\Delta n(t) = n_2 - n_1$ and $N = = n_2 + n_1$ in the form of:

$$\Delta n(t) = N\left(1 + \frac{2}{N} e^{-w_{12} t}\right).$$

For the every transfer step lasting τ, that is at $N = 1$ (an excess electron is in the position 1 or 2) and $\Delta n = 2$ (the transfer increases n_2 by one and decrements n_1 by one) we obtains the simple ratio $w_{12} = -\ln 2/\tau$. The ratio exactly corresponds to the first-order reaction kinetics, if you think that $\tau = \tau_{1/2}$ — electron donor semi-oxidation period, and w_{12} — donor-acceptor electron-transfer rate (frequency F). Hence for the electron transfer frequency in the terminal section of line that is equal to $F = 1/\tau = 1.7 \cdot 10^3\,\mathrm{s}^{-1}$, we find $\tau = 5.8 \cdot 10^{-4}\,\mathrm{s}$ and the electron transition count per second $w_{12} = 1.2 \cdot 10^3\,\mathrm{s}^{-1}$ correspondingly.

Free energy change is determined by the sum of the energy E_a, essential for generation of the activated complex on the donor level (cytochrome oxidase $a + a_3$), and the energy ΔG, released during the electron transfer to the acceptor level $(1/2)\mathrm{O}_2$). Thus the following ratio is fulfilled:

$$w_{12} = \frac{\omega_0}{2\pi}\exp\left(-\frac{E_\mathrm{a}}{k_B T}\right) \cdot \exp\left(\frac{\Delta G}{k_B T}\right).$$

The activation energy E_a during oxidoreduction of the component $a \to a_3$ approximates to $E_\mathrm{a} = |0.29 - 0.55| = 0.26\,\mathrm{eV}$. The calculation gives the value of the first multiplier equal to $\exp(E_\mathrm{a}/k_B T) = \\ = 4.54 \cdot 10^{-5}$ $(k_B T = 0.026\,\mathrm{eV})$. The difference of the redox potentials of the component $a_3 \to (1/2)\mathrm{O}_2$ is $\Delta G = 0.55 - 0.82 = -0.27\,\mathrm{eV},$ and the value of the second multiplier is equal to $\exp(\Delta G/k_B T) = 3.1 \cdot 10^{-5}$. correspondingly. Note (we record) that oxidoreduction of both components of the chain, $a \to a_3$ and $a_3 \to (1/2)\mathrm{O}_2$ proceeds, as noted above, approximately at the same rate (the semioxidation time $\tau_{1/2}$ is equal to 0.51 ms и 0.4 ms). Further we shall calculate at $\omega = 10^{13} \div 10^{14}\,\mathrm{s}^{-1}$ the electron transition value (the frequency) $w_{12} = \\ = 2.24(10^3 \div 10^4)\,\mathrm{s}^{-1}$, answering enough the value calculated earlier by the differential transfer equation solution.

SHORT CONCLUSIONS

The studies of the biological membrane conductivity, as well as of many other membrane physical parameters, are in place in the common process of biology and electronics convergence. By 2009 it was pointed out [25] that the area of bioelectronics has been adequate to exponential growth. Biological membranes are already commonly used as sensors for diagnostic purpose in respect of many diseases, for

DNA, proteins and cell metabolites rapid analysis; as component of thin-film techniques and in another applied directions. The number of such directions will quickly increase.

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