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JÓZEF ZON

ELECTRONIC CONDUCTIVITY IN BIOLOGICAL MEMBRANES

The ionic conductivity across biological membranes has long been a subject of investigation and its significance for basic physiological processes in many respects has been ascertained. However, the possibility of electronic conduction in these membranes continues to be a subject of considerable controversion. This type of conductivity may be realized in the molecular structures of biomembranes by one of the following ways:

i) tunelling across intra- and intermolecular energy barriers ⟨Eley 1962; De Vault et al. 1967; Floyd et al. 1971; Chance 1975; Hopfield 1977; Petrov et al. 1979; Chernavskij et al. 1982⟩,

ii) activated hopping of electrons over these barriers — so called exciton mechanism ⟨Fröhlich, Sewell 1959; LeBlanc 1962⟩,

iii) conduction along common energy bands ⟨Szent-Györgyi 1941; Brillouin 1962; Pethig 1977; Ladik 1979⟩.

Semiconductivity of chemical compounds isolated from biological structures has been reviewed many times ⟨e.g. Gutman, Lyons 1967; Rosenberg, Postow 1969; Boguslavskii, Vannikov 1970; Meier 1974; Cope 1975; Frnst 1975; Pethig 1977; Simionescu et al. 1978; Pethig 1979; Simionescu, Percec 1980; Kryszewski 1980⟩. It has been proved that proteins, lipids, and nucleic acids, when investigated in vitro, may behave as electronic conductors. This same may be said about more composite biological materials, as macromolecular complexes of some cells and organelles and extensive fragments of some tissues.

It is, however, problematic whether these materials may also function as electronic conductors during normal physiological activity. In order to approach the answer to the question, it has been resolved to review the papers describing characteristic features of semicon ductor behaviour in biological membranes. To make the survey more complete, along with experimental results, some theoretical considerations also have been taken into account.

An electronic semiconductor is characterized by the following features ⟨Kryszewski 1980, p. 2⟩:

i) electric conductivity in the range from 10^{-10} to 10^{6} mho-m^{-1},
ii) positive temperature coefficient of conductivity,
iii) non-ohmic and often rectifying action in contact with other conductors, especially metals,
iv) high values of thermoelectric force, the sign of which does not depend on the type of metal brought into contact with the semiconductor,
v) photoconductivity,
vi) the dependence of conductivity on the type and amount of impurities.

Usually, as a criterion for semiconductivity of the material the compliance with the requirement (ii), described by the following formula is used:

$$\sigma=\sigma_0\exp[-E_g(2kT)^{-1}] \quad (1)$$

where:

σ — the observed value of conductivity (mho),
σ_0 — a constant, dependent mainly on the mobility and effective mass of charge carriers (mho m^{-1}),
E_g — the energy gap (J),
k — Boltzmann's constant (J K^{-1}),
T — absolute temperature (K).

Whereas this type of thermal behavior of conductivity may also be found in dielectrics, it is assumed that the value of E_g in semiconductors should be lower than 3 eV ($5{,}4\times10^{-19}$ J). Moreover, the other properties listed above should be also ascertained in the material to classify it as an electronic semiconductor.

One of the earliest suggestions of electron transfer across biological membranes was made by Lund ⟨1928⟩. He proposed that the membrane was a structure coupling two redox systems placed on both sides of it (an electrostenolytic system). The idea was relinquished for many years, because it was belived that there are no molecules in the membranes, which may function as „wires" carrying electronic currents. A new momentum was given to the idea, when it has been discovered that many biologically active compounds can act as electronic semiconductors. The Lund's idea was undertaken by Jahn ⟨1962⟩ who ascribed the role of wires spanning the biological membranes to carotenoids — molecules possessing systems of conjugated bonds. The generation of free electrons for the conduction across the membranes was ascribed to the action of ATP. The electromotive force, driving the electrons along these bonds, was supposed to be generated due to the differences in the electronic pressure between both sides of the membrane.

The research on the electronic conduction across biological membranes in the solid-state physics perspective began in the middle of the sixties and up to now has covered all main types of these structures. Paralelly with these efforts, a new field of the research dealing with electronic conduction in models of natural membranes — the bilayer lipid membranes (BLM) — was open in the late sixties. This new field remarkably supplements the research done on natural systems, and makes the conclusions drawn on the properties of natural membranes more reliable. Extensive reviews of this area of the study have been given by Rosenberg ⟨1971⟩ and Tien ⟨1972, 1973, 1974, 1979⟩.

This paper has been divided into two main parts. In the first one, the electronic conduction in the membranes physiologically active in the dark are presented; in the other one — the electronic properties of membranes functioning as phototransducers have been described. In the latter case special attention is paid to the photoelectric effects in natural membranes.

1. ELECTRONIC PROPERTIES OF THE MEMBRANES PHYSIOLOGICALLY ACTIVE IN THE DARK

1.1. *Secretory cells and erythrocytes*

In 1970, Mandel when investigating the relation between the voltage and current flowing across the membranes of several types of secretory cells of animals, suggested that the most adequate approach to the nature of these processes is to assume an electronic current flowing across semiconducting membranes which divide different solutions. Pohl and Sauer ⟨1978⟩ have arrived at similar conclusions when investigating electrostenolytic effects taking place across the salivary gland of the Lone Star tick. However, both the research done by the authors mentioned above, and Digby ⟨1964⟩ are not to be directly referred to cell membranes, because the membranes of secretory cells are very thick (up to several hundred nanometers) and composite structures.

The electron flow across the membranes of erythrocytes was discovered by Marinov ⟨1979⟩. To oxidize hemoglobin in the interior of these cells, he exposed the erythrocytes to the action of hydroxylamine. Next, the erythrocytes were incubated in the solution containing eosine and NADH, and the suspension was illuminated with the visible light. In the result, a shift of the Soret band has been found and a new absorption band in the range of 540-580 nm was brought about. These changes were interpreted as indicative of the reduction process having taken place inside the cells. Connected with the reduction, the oxidation of complexes of eosine with NADH outside the cells was found. Considering both types of reactions, ascertained simultaneously on both sides of the erythrocyte membranes, the investigator concluded that transfer of electrons across the membranes took place. In additional experiments, involvement of membrane permeable electron carriers has been excluded. The role of the medium conducting electrons across the erythrocyte membrane was ascribed to giant protein molecules of spectrin.

1.2. *Muscle cells*

In the membranes of muscle cells, three types of effects characteristic of semiconductors were discovered: the exponential increase of conductivity with rising temperature; the thermoelectric force generation, and photoconductivity. The conductivity changes, fitting in Equation (1), have been found in dried muscle fibres ⟨Lakatos 1962⟩, and in fresh frog muscle ⟨Nagy 1970⟩. In the latter case, the exponential changes of conductivity took place in the temperature range 289-297 K. When the temperature was brought above 297 K the conductivity did not change, and above 312 K — its value dropped. The value of E_g, calculated on the assumption of validity of Eq. (1) was about 2 eV. It has not been determined whether the current carriers were electrons or holes.

The generation of differential thermoelectric force in the muscle of the frog was found by Lakatos and Kollar-Morocz ⟨1969⟩. The value of this force was calculated to be 230 ± 40 $\mu V\ K^{-1}$. The holes have been found to be the dominant current carriers in the temperatures below 292 K, and the electrons — above 298 K. The ability to generate the thermoelectric force ceased, when the muscle had been treated by chloroform.

The photoelectrically mediated action of the light on the heart of the frog was demonstrated by Lakatos and Kollar-Morocz ⟨1966⟩. In their experiment, the beating of isolated hearts was stopped by depletion of K^+ ions form the bathing Ringer solution. When to this solution Na-eosine was added and an intense light was used to illuminate the hearts, the beating recured more frequently than in the nonilluminated ones. Slight rise of temperature (of about 1 degree) was accounted not to be significant in causing these changes. Instead, the investigators pointed to the possibility that the action of the light caused an electronic excitation of eosine. In the next step, the electrons were supposed to move along the π-bonds systems of the molecular structures of the membranes, which eventually lead to the increase of the probability of recurence of heart beating. Similar type of causal connection was suggested by thes same investigators ⟨Lakatos, Kollar-Morocz 1967⟩ for the decrease of the threshold of excitation of eosine- and light-treated muscle cells.

1.3. *Neurons*

E. Ernst ⟨1955/1956⟩ was the first who tried to connect the functions of nerve cells with the properties of semiconductors. Among other similarities in behavior of both semiconductors and neurons, he mentions the reactions to temperature changes and to contaminations. This author saw also essential similarities in functioning of the p-n semiconductor junction and the modulation of the nerve impulse ⟨Ernst 1956⟩. These precursory and simplified analogies drawn by Ernst have been criticized by Liberman ⟨1958⟩, who put also some suggestions concerning further research on semiconductivity in nervous system.

Blocking of the action potentials in the Pacinian bodies by procaine and thioguanine, he considers as a manifestation of the stopping of the flow of free electrons in the neuron membranes ⟨Ernst 1966⟩. In a similar way he explained the action of veratrine and novokaine ⟨Ernst 1968⟩.

On the basis of formal similarity between high-frequency oscillations in the Gunn's diode, Ernst ⟨1968⟩ proposed that the frequency modulation in some nerve cells was brought about by a mechanism similar to that one active in the Gunn's diode.

The photocurrent and photovoltage generation was found in stained giant axons of Aplysia ⟨Chalazonitis 1964⟩. The sign of the photopotential generated in the membrane has been shown to depend on the type of dye used for staining, and its concentration in the membrane. The measure of the influence of light on the membrane was the rate of the depolarisation taking place in the first second after the beginning of illumination. The rate of depolarisation, dV/dt, was shown to change accordingly to the formula:

$$\frac{dV}{dt} = A \exp(kt) \tag{2}$$

where:

A and k are constants dependent on the intensity of light at a given wavelength, temperature, polarisation of the membrane, and the partial pressure of oxygen,

t is the time lapse after beginning of illumination.

If the intensity of the light at a given wavelength reached certain value, rhytmical nerve firing was brought about. The densities of the surface photocurrent were evaluated to be about 60 mA/m^{-2}. In discussion of the results of the experiments, the attention was paid to the role of electronic excitation and transfer of electrons. It has been hypothetized, that after the illumination causing electronic excitation in the dye molecules, free electrons or holes should be created. These charge carriers, along with protons, before trapping in the final acceptors, were thought to depolarize the membrane. Cope ⟨1968⟩ showed that the Chalazonitis' results may well be interpreted as displaying behavior typical to the generation and decay of free charge carriers in semiconductors, described by the kinetic Elovich equation.

In 1962, Kirzon et al., observed an exponential drop of impendance in the sciatic nerve of the frog caused by illumination. As a possible explanation of the results they obtained, the semiconductivity of the components of the nerve membrane was suggested. If the neurons were stained either with eosine, or bengal rose, or with neutral red, and then illuminated, the firing activity was generated ⟨Lakatos 1969⟩. In spite of the fact that less than in 50⁰/₀ of stained neurons the activity was observed, the activity did not occur neither in stained but non-illuminated, or in unstained and illuminated. These results were explained in a similar way as the Chalazonitis' ones. In earlier experiments ⟨Ludvikovskaya, Pangloleva 1965⟩, the firing of neurons was shown to be generated even in unstained neurons, when they were illuminated with ultraviolet ($\lambda=260$, 280, 313 nm) or visible ($\lambda=405$ nm) light and the temperature kept between 279 and 283 K. The neurons did not respond to the light when the temperature was in the range of 293 to 295 K.

On the basis of earlier suggestions made by Ernst, Nagy et al. ⟨1978⟩ investigated the relationship between the temperature and the velocity of the propagation of the excitation in the sciatic neuron of the frog. They found that in temperatures between 278 and 303 K, the velocity of the spike propagation increased linearly. The increase was not exponential, as demanded by Eq. 1. Therefore, it cannot be regarded as directly connected with possible exponential rise of electronic conductivity.

Finally, the generation of thermoelectric power in the neuron was discovered ⟨Lakatos, Kollar-Morocz 1969⟩. The thermoelectric coefficient was evaluated to be 45 ± 15 $\mu V\ K^{-1}$. Its value decreased with time, and completely ceased after 9 days of preservation of the nerve.

1.4. *Mitochondria*

This subcellular structure is the main source of ATP in the cells of aerobic organisms. Before mitochondrion was identified as the „power plant" of cells, A. Szent-Györgyi ⟨1941⟩, following earlier suggestion made by P. Jordan ⟨1938⟩, had hypothetized that transport of energy in the cell involves a similar mechanism as that found in some electronically conducting solids. According to this hypothesis, in insoluble proteins, common energy bands occur, and the energy transport takes place when electrons move along these bands. This suggestion gave rise to numerous works devoted to the investigation of semiconductivity in biological materials.

Vannikov and Boguslavskii ⟨1969⟩ estimated the mobility of free charge carriers in films made of mitochondria. The value of μ was about 5×10^{-6} m^2 V^{-1} s^{-1} in samples hydrated in less than 1%. In protein-lipid extracts from mitochondria, the mobility of electrons was found to be about 2 orders of magnitude higher ⟨Eley, Pethig 1971⟩. However, if these investigators took into account a correction for the space involved in measured conductivity, they concluded that the actual values of μ should be even 10 times higher than previously estimated. The thermoelectric force generation in pressed pellets of mixture of intact mitochondria with submitochondrial particles was investigated by Eley et al. ⟨1977⟩. They found that in temperatures below 342 K, electrons are the dominant charge carriers and holes — above this temperature.

1.5. *Non-photosynthetizing plant cells*

Skierczyńska et al. ⟨1970⟩ observed that immersion of algal cell in water caused 50% reduction of longitudinal impedance of this cell. As the possibility of the influence of outward currents flowing across the cell membrane had been excluded, participation of electronic currents in membranes was suggested. To test this possibility, an attempt at detecting the Hall voltage generation in the wall and membrane of the cell of Nitellopsis obtusa was made ⟨Skierczyńska et al. 1977⟩. The induction of the magnetic field used in the experiments ranged from 0.8 to 2.0 T. The currents generated across the wall and cell membranes were from 1.3 do 2.2 μA. In spite of considerable difficulties, the Hall's voltages from 100 to 650 μV were detected in living cells. No Hall's voltage generation was found in the dead ones.

Changes of resting potentials in plant cells under the influence of light are known phenomenon ⟨cf. Hansen et al. 1973⟩, and these responses are not directly influenced by light. Namely, in evoking them, the metabolic activity dependent upon the influence if light upon the chloroplasts is involved. This not withstanding, a direct action of light on the plant cell membrane is possible. It has been demonstrated on rhisoids of some algae, where chlorophyll occurs in extremely small quantities ⟨Adrianov 1970⟩. Similar observations were reported earlier by Bose ⟨1907 p. 396⟩ and Waller ⟨1925⟩.

Using ultraviolet light, Bulanda and Pałczyńska ⟨1976/1977⟩ were able to detect a direct action of this light on cell membranes of algal cells. This action manifested itself in fast changes ($\leqslant$ 1 sec) of the resting potential (U≈3.5 mV). The possibility that these changes were brought about by the absorption of ultraviolet by lipids and proteins was considered to be of minor significance.

2. ELECTRONIC PROPERTIES OF THE MEMBRANES PHYSIOLOGICALLY ACTIVE IN THE LIGHT

2.1. *Light receptors*

Dried rods of the eye of the sheep were shown to be photoconductive and follow the conductivity changes in accord with Equation 1 by Rosenberg et al. in 1961. The value of E_g was calculated to be about 2.3 eV. More rigorous measurements, avoiding the problems connected with using steady currents, were carried out by Trukhan et al. ⟨1970⟩ on pigment epithelium of the eye of the frog. Applying high frequency currents, they showed that photoconductivity is proportional to the intensity of light and water content in the samples. The holes were indentified to be the charge carriers. Their Hall mobility was estimated to reach 1.5×10^{-3} m^2 V^{-1} s^{-1}. Falk and Fatt ⟨1967⟩ measured the admittance of rod segments in the frequency range from 15 Hz to 60 kHz. In discussing the mechanisms underlaying the observed admittance changes, they saw electronic conduction to be an option to the protonic movement along the membranes.

One of the features of the involvement of electrons in a response to an external agent is a very fast change of voltage or current across the membrane. The most spectacular changes of this type were observed in the so called early receptor potential (ERP).

ERP was discovered by Brown and Murakami in the retina of the monkey in 1964 ⟨1964a⟩. This response was found in visual receptors of invertebrates ⟨Brown 1965; Brown, Gage 1966; Crawford et al. 1967; Hagins, McGughy 1967⟩ and other vertebrates ⟨Brown, Murakami 1964b; Pak 1965; Cone, Cobbs 1969⟩. ERP consists of three phases of potential changes, the last one being identical with the α-wave of electroretinogram. The first two phases, the positive and negative one, have been shown to be independent of the ionic current, flowing across the membrane, on the following grounds:

i) they are not changed by anoxia ⟨Brown, Murakami 1964a⟩,
ii) they occur even if the ionic environment of the membranes has been changed ⟨Pak 1965; Brindley, Gardner-Medvin 1966; Crawford et al. 1967⟩,
iii) the lowering of temperature does not abolish the positive phase, but it reversibly changes the negative one ⟨Pak, Cone 1964; Pak, Ebrey 1965; Brown, Gage 1966⟩. However, increasing the temperature of re-

tina above 321 K or cooling to 188 K and subsequent thawing it ⟨Hagins, McGughy 1967⟩, abolishes the photoresponse of retina. This damaging action of high or low temperatures is believed to be caused by damages of molecular organisation of the membranes,

iv) fixation with glutharaldehyde or formaldehyde abolishes only the third, ion-dependent phase, but only slightly changes the course of the first two ones ⟨Brindley, Gardner-Medvin 1966; Hagins, Mc Gughy 1967; Arden et al. 1968⟩,

v) the fast positive phase does not vanish even in dehydrated pigment cells ⟨Brown, Gage 1966⟩,

vi) the responses to light of retina and of silicon photocell having identical passive electrical properties as retina are indistinquishable ⟨Arden et al. 1966⟩.

The mentioned above evidence for non-ionic nature of the first two phases of ERP have lead some investigators ⟨Brown, Gage 1966; Brown, Crawford 1967; Crawford et al. 1967⟩ to consider first stages of photoreception in terms of solid state electronics.

2.2. *Chloroplasts and chromophores*

The first authors to raise the idea that energy conversion and transport may involve conduction of electrons along common energy bands were Möglich and Schön ⟨1938⟩. Many experiments have been carried out to explore this new, based on solid state physics, perspective in biophysics of photosynthesis.

The conductivity changes in dried chloroplasts following Eq. 1 and photoconductivity have been reported by many investigators ⟨Arnold, Sherwood 1957; Arnold, McLay 1958; Ichimura 1960; Zvalinskii, Litvin 1967; Litvin, Zvalinskii 1971⟩. Another approach was chosen by McCreé ⟨1965⟩ to investigate photoconductivity in chloroplasts. Using a condenser method, allowing the detection of currents 10^3 times weaker than those found in inorganic photoconductors, he was not able to find photoconductivity either in dried chloroplast layers, or in monolayers of chlorophyll and proteins. Attempts to find photoconductivity in dried green algae or higher plant leaves were also unsuccessful. On the basis of these results, McCree concluded that even if photoconductivity occurs in plant material, it cannot be regarded as an efficient mechanism of light energy conversion in photosynthesis.

Zvalinskii and Litvin in 1967, using a sensitive electrometer, found that the action spectrum of photoconductivity and absorption spectrum coincide with each other in visible region. In the infra-red, the photocurrent was also generated with maxima lying at 950, 1040, 1260, and

1550 nm. This coincidence of spectra and the occurence of maxima in infra-red action spectrum, point to the chlorophyll molecules and aggregates of them, as playing a crucial role in photoconductivity of chloroplasts. In a more rigorous study ⟨Litvin, Zvalinskii 1971⟩, it has been found that the action spectrum of photoconductivity coincides with the resultant absorption spectrum of main photosynthetic pigments present in chloroplasts. Both the dark and the conductivity under illumination followed Eq. 1 in temperatures between 253 and 293 K. The specific dark conductivity of chloroplasts was calculated to be of the order of 10^{-11} to 10^{-10} mho m^{-1}, and $E_g \approx 1.72$ eV. The drift mobility was estimated to be between 1×10^{-5} and 1×10^{-3} $m^2 V^{-1} s^{-1}$.

The generation of free charges in chloroplasts and the membranes of photosynthetic bacteria has also been investigated, using measurements of dielectric losses, ε'', at microwave frequencies. Blumenfeld et al. ⟨1970⟩ showed that ε'' in leaves and chloroplasts extracted from sorghum and broad bean parallels the absorption spectrum of chlorophylls, a and b, and probably, β-carotene. Although the action spectra of both native leaves and extracted chloroplasts were qualitatively similar, the action spectra of native leaves were 5—7 times stronger. The microwave photoconductivity signal depends on the functional state of photosynthetic membranes. When chloroplasts are fresh and intact, the response is biphasic, and if they are old or damaged (e.g. by heating), the response in monophasic ⟨Blumenfeld et al. 1974; Deryabkin et al. 1978⟩. To ascertain the possible electron involvement in generation the observed dielectric losses, a model system was used. Is consisted of a suspension of photoconducting ZnO particles, illuminated with the light, $\lambda = 380$ nm. The photoconductivity signal of these electronically conducting particles and chloroplasts was alike ⟨Deryabkin et al. 1978⟩.

Bogomolni and Klein ⟨1975⟩ combined the microwave photoconductivity measurements with Faraday rotation measurements on films of dried intact and broken chloroplasts from spinach and algae as well as on the chromophores from photosynthetic bacteria. They found that photoconductivity signal was generated by both negative and positive carriers. The negative ones seemed to be released thermally from the primary acceptors, the positive carriers having been identified with the movement of dimeric chlorophyll cation radicals. The Hall mobilities of charge carriers and their density were calculated to be the order of 1×10^{-4} $m^2 V^{-1} s^{-1}$ and 10^{19} m^{-3}, respectively. The data obtained in these measurements seemed to give support for the tunneling or hopping mechanism of charge migration, instead of conduction along common energy bands.

The microwave conductivity in reaction centers of photosynthetic bacteria has been shown ⟨Skachkov et al. 1980⟩ to consist of two components characterized by different rates of rise. The first one, conceivably having its cause in the migration of electrons between quinones, builds up very fast ($\leqslant 1$ s) and the other one develops slowly (≈ 20 s). The amplitude of the fast response depends strongly on the level of hydration, and rises with its increase. The investigators, having in mind the dependence of microwave conductivity on the hydration degree, suggested that the presence of water influences the mobility and population of electrons in conduction bands of proteins in reaction centers. On the other hand, the slow component was interpreted as reflecting the accumulation of mobile electrons in electron transport chains and/or changes in the charge distribution in the photosynthetic apparatus.

The emission of the so called delayed light, discovered by Strehler and Arnold in 1951, is interpreted by some authors as a manifestation of electron migration and trapping in energy bands of semiconductive photosynthetic structures. Tollin and Calvin ⟨1957⟩ investigated the dependence of the delayed light intensity on temperature, down to 133 K. Because the free radical recombination and emission from triplete states had been excluded, the authors explained their results in terms of electron trapping and subsequent recombination of electrons and holes, giving rise to luminescence. Similarily, enzymatic reactions have been also excluded, because their rate at low temperature was incompatible with the delayed light intensity ⟨Tollin et al. 1958; Calvin 1958; Litvin, Shuvalov 1968⟩. If an external electric field had been applied, the intensity of delayed luminescence rose about 50 times ⟨Arnold, Azzi 1971; Arnold 1972⟩. This increase was interpreted as caused by electric field enhancement of the rate of detrapping of electrons and their recombination. The depth of perticular charge traps localized in the forbidden energy band, was studied by measuring the time or temperature distribution of the intensity of lelayed light ⟨Litvin, Shuvalov 1968; Arnold 1977⟩.

The whole process leading to the generation of the delayed luminescence is believed to consist of the following stages ⟨Arnold, Sherwood 1959; Arnold 1965; 1977⟩:

i) translocation of electrons to the conduction band,
ii) trapping them on the energy levels lying close to the bottom of the conduction band,
iii) thermally evoked release of trapped electrons to the conduction band,
iv) reversion of electrons to the valence band, connected with their recombination with holes and light quanta generation.

This relatively simple picture of the mechanism of the generation of delayed luminescence has been supplemented by the processes of trapping of holes, creation of radicals by the energy released on the traps, and finally, generation of chemically stable compounds ⟨Calvin 1958; Arnold, Azzi 1968). Although this general idea of semiconductor processes involvement in the generation of delayed luminescence may essentially be correct, it is considered to be an oversimplification. Malkin's review (1977) discusses other mechanisms of the delayed light generation, competing with the semiconductor approach. Another group of experiments revealing the electron transfer in the membrane present the investigations of the shifts in absorption spectra (electrochromism) of chloroplast pigments (Junge, Witt 1968; Witt, Zickler 1973). Their study suggests this electron transfer probably does not take place perpendicularily to the membrane surface (Junge, Witt 1968) and is very fast ($<$ 20 ns) (Wolf et al. 1969). These fast electron movements and following much slower relaxation processes may well be compatible with the semiconductor model of photosynthesis.

To find in which direction the electrons are transfered in illuminated chloroplasts, Fowler and Kok (1974) investigated the electric field generation in suspension of chloroplasts. It has been found that the chloroplasts charge negatively on the illuminated side and positively on the dark one when illuminated with a very short pulse of light. The rise time of the photopotential was shorter than 1 μs. Similar results have been obtained by Nobel and Mel (1966) who investigated the changes of mobility of chloroplasts caused by their illumination. They found that continuous illumination of chloroplasts charges them negatively and causes about 15% increase in their mobility. These authors argued that the involvement of some mechanisms of solid state physics seems very probable in causing these effects, since they did not occur when membranes of chloroplasts have been damaged.

Fast ($< 10^{-2}$ s) and positive charging of the inside of chloroplasts was described by Bulychev et al. (1971, 1972) and Vredenberg and Bulychev (1976), who used microelectrodes to measure these changes. Finally, it is worth mentioning here that a response similar to ERP was detected in leaves of the gout weed (Arden et al. 1966). This may be understood as another evidence for close connection between the displacement and flow of electrons in pigmented cell constituents and their natural responses to light.

3. CONCLUDING REMARKS

Biological membranes may be regarded as ultrathin, double layers composed of solid particles (mainly proteins) and liquid crystals (lipids). The results of investigations reviewed above, show that in aggregates of molecules building up the biological membranes free electrons may occur. Taking into account the occurence of such semiconductor properties as:

positive temperature coefficient of conductivity, the values of forbidden energy gap and conductivity lying in the range characteristic of semiconductors, measurable Hall effect and photoconductivity, one may depict living organisms as systems penetrated by extremely ramified, ultrathin and highly differentiated membraneous semiconducting material.

Regarding the discrepancy between the complexity of biological membranes and methodology used for detecting the electronic currents in these structures, it must be said that the results reviewed in the paper may also be subject to interpretation in terms of ionic conductivity and polarization phenomena. However, in most of the experiments mentioned above, the attention was paid to exclude these possibilities. Moreover, experiments with models of biological membranes ⟨Rosenberg 1971, Tien 1979⟩, often carried out to obtain cheap and efficient photocells ⟨Calvin 1974, 1978⟩, make the electronic conductivity in biomembranes a very plausible possibility.

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ELEKTRONOWE PRZEWODNICTWO W BŁONACH BIOLOGICZNYCH

Streszczenie

W artykule dokonano przeglądu tak ogólnych argumentów, jak i danych uzyskanych eksperymentalnie, świadczących o elektronowym przewodnictwie w błonach biologicznych. Głównymi racjami teoretycznymi świadczącymi za zaangażowaniem przewodnictwa elektronowego w błonach są: 1. w łańcuchach biochemicznych reakcji redoks zachodzi transfer elektronów między molekułami, czasami na znaczne odległości, jak ma to na przykład miejsce w elektrostenolizie, 2. wysoce uorganizowane struktury supramolekularne błon, jeśli same są badane in vitro i wykazują wtedy własności półprzewodnikowe, powinny również wykazywać te własności w warunkach fizjologicznych, 3. jest prawdopodobne, że w elektronowym przewodnictwie przynajmniej jeden z podanych mechanizmów jest czynny: a) tunelowanie, b) ekscytony, c) przewodnictwo wzdłuż pasm wspólnych energii.

W płaszczyźnie eksperymentalnej następujące efekty mogą być uważane za te, które wskazują na prawdopodobne przewodnictwo elektronowe w błonach: 1. wykładniczy wzrost przewodnictwa wraz z temperaturą, 2. efekty fotoelektryczne i zmiany termiczne przewodnictwa wskazujące, że wartość E_g powinna być mniejsza niż 3 eV, 3. efekty termoelektryczne, 4. bardzo szybkie reakcje elektryczne na puls światła, które nie zgadzają się z mechanizmem jonowym tych zmian, 5. mierzalne napięcia Halla.

Pomijając mitochondria, chloroplasty i receptor wzroku, fizjologiczna rola prądów elektronowych w błonach nie jest jasna w dalszym ciągu. Jest także wątpliwe czy pewne zjawiska, które wyjaśniano w kategoriach prądów elektronowych, nie mogą być wyjaśnione poprzez prądy jonowe. W związku z tym bardzo ważny wgląd można uzyskać przez badania nad elektronowym przewodnictwem układów modelowych znanych pod nazwą podwójnowarstwowych (czasami: czarnych) błon lipidowych (BLM).