

The Semiconducting Diode Behavior of Bimolecular Lipid Membranes

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Many biological membranes show a marked non-linearity in their current–voltage curves. There has been much speculation concerning the nature of these membranes, in particular, nerve membranes, and the manner in which the ionic conductances through this membrane are dependent upon the applied voltage. However, the molecular bases of the voltage-dependent ionic permeability is still not clear. The artificial bimolecular lipid membranes provide a good model system for studying a number of properties of the cell membranes. In particular, it is an excellent system for investigating their electrical properties. In recent years a number of papers on this subject have appeared, each suggesting different mechanisms of conduction through the bilayer. Ionic transport has been suggested by Liberman and co-workers¹ and Finkelstein *et al.*² A protonic conduction has been postulated by Thompson and Lehninger³ and others. On the other hand an electronic component has been indicated by Lauger and co-workers⁴ and Rosenberg and co-workers.⁵ The details of the mechanisms are different in each case.

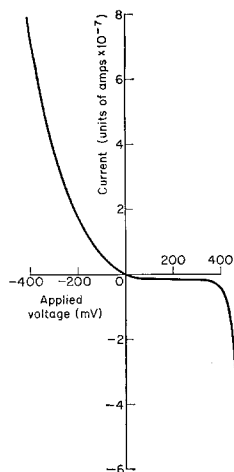
Rectifying behavior of the current–voltage (I/V) curves of phospholipid membranes separating solutions of 3 M KCl and 1 M KI has been reported by Pasharyev and Tsofina.⁶ Rosenberg and Pant have suggested that an oxidized cholesterol bilayer membrane behaves as a semiconducting rectifier in the presence of various acceptors, e.g. iodine, picric acid, 2,4 DNP, TNB, safranin etc.⁷ In this report, we discuss some studies on the nature of the I/V curve of egg lecithin and oxidized cholesterol membranes separating compartments containing solutions of oxidizing and reducing species. It is noted, that with a proper selection of these compounds which could interact with the membranes, a large rectification effect across the membranes can be obtained, with the forward direction being negative charges moving from the donor (reducer) side to the acceptor (oxidizer) side.

Bilayers of egg lecithin were made as described in the earlier work. The outer compartment of the teflon cup containing water or dilute KCl solution is flushed with nitrogen for several minutes before adding ferrous chloride solution. The inside cup contains a high concentration (5×10^{-3} M) of ceric ammonium sulphate. Ceric ammonium sulphate alone increases the conductance of the egg lecithin membrane by two orders of magnitude, and shows a rectification effect in the direction of the negative charges moving from the water compartment to the ceric compartment. On adding the ferrous chloride solution to the outer cup, the conductance is further increased by three orders of magnitude and the membrane exhibits a large rectifying behavior. Both compartments were

well stirred. A ramp voltage of very small frequency (0.2 Hz) from an Ando oscillator is then applied, through a $1\text{ M}\Omega$ resistance, to the outer cup electrode (containing ferrous chloride), and the inner cup electrode (containing ceric ammonium sulphate) is connected to the electrometer using the low resistance range. The output of the electrometer is connected to the y -axis, and the output of the applied voltage is connected to the x -axis of a Moseley x - y recorder. A trace of the resulting I/V curve is shown in Fig. 1. At lower applied potentials (20 mV to 350 mV) the I/V curve shows a large rectification effect, with the forward direction being that of the negative charges moving from the ferrous compartment to the ceric compartment.

As the magnitude of the applied potential is increased, a sudden large increase in the current in the back-rectifying direction is observed. The value of this "breakdown" potential for the egg lecithin membrane with $5 \times 10^{-3}\text{ M}$ ceric ammonium sulphate and $\approx 10^{-2}\text{ M}$ ferrous sulphate is $\approx 450\text{ mV}$ (Fig. 1). This observation is quite reproducible

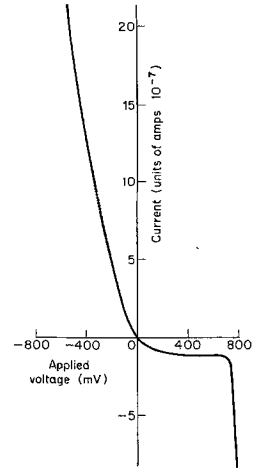
Figure 1. A current versus applied voltage curve for a bimolecular lipid membrane formed from egg lecithin in decane separating ceric ammonium sulphate ($\sim 10^{-3}\text{ M}$) and ferrous chloride ($\sim 10^{-3}\text{ M}$) solutions.



with a number of different membranes having the same composition. On any one membrane this curve can be retraced indefinitely. The sharp increase of current is not a destructive breakdown. While we cannot as yet eliminate the possibility of a "puncture breakdown" due to the applied electric field strength exceeding the dielectric strength of the membrane, it is obvious that any such puncture must be rapidly self healing for repetitions of the curve to be run. The self e.m.f. generated across the membrane is -70 mV . Similar I/V curves have been obtained for a phosphatidylethanolamine-oxidized cholesterol (1:4) bilayer, however the "breakdown" voltage in this case is 700 mV (Fig. 2).

We have found that the current-voltage relationship is logarithmic, rather than linear, at higher applied voltages ($\geq 100\text{ mV}$) in the case of egg lecithin and phosphatidylethanolamine membranes. These non-linear characteristics can be considered due to non-linear rate processes. The rate determining step for the passage of a predominantly electronic current is the transfer of electrons across the interface between one of the solutions and the membrane. The observed large rectification effect in the presence of certain oxidizing

Figure 2. A current versus applied voltage curve for a bimolecular membrane formed from a mixture of phosphatidylethanolamine and oxidized cholesterol in decane separating ceric ammonium sulphate ($\sim 10^{-3}$ M) and ferrous chloride ($\sim 10^{-3}$ M) solutions.



and reducing chemicals separated by the membrane is suggestive evidence for the predominance of electronic charge carriers.

The "breakdown" voltage of the I/V curve for any given membrane depends on the temperature of the bathing solution; with an increase in temperature the "breakdown" voltage decreases. Concomitantly there is an increase in the magnitude of the current and a decrease in the rectification ratio. At 25°C the value of the "breakdown" voltage is 450 mV, while at 35°C it decreases to about 250 mV (Fig. 3). We do not have a good explanation at the present for this phenomenon of "breakdown" potentials. However, these types of current-voltage characteristics are quite common in semiconductor diodes due to depletion of a space charge region. One possible explanation for the effect in membranes, therefore, is that a space-charge region is formed at the interfaces due to the coupled reactions. This suggests that an egg lecithin membrane could be behaving like a semiconductor diode. In such semiconducting diodes, two distinct voltage breakdown

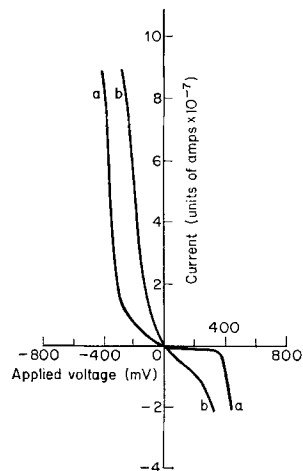


Figure 3. A current versus applied voltage curve for an egg lecithin bimolecular lipid membrane separating ceric ammonium chloride and ferrous chloride solutions; (a) at 25°C and (b) 35°C .

mechanisms are known to occur, "avalanche breakdown" and "Zener breakdown". These may be operationally separated, since in the former case the "breakdown" voltage increases with increasing temperature, while in the latter case, the "breakdown" voltage decreases with temperature. The data of Fig. 3 indicates that the effects in the membranes are more closely related to the "Zener breakdown".

Acknowledgements

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