Anomalous Conduction across Ion-exchange Membranes

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It is extensively shown that a constant electric current passes across ion-exchange membranes under normal conditions, when a constant voltage being applied. Sometimes, however, the anomalous conduction phenomena are observed; that is, non-ohmic conduction and pulse generation[1,2]. The aim of the present communication is to clear the conditions under which the anomalous conduction takes place and to propose a mechanism for pulse generation.

Anomalous conduction is observed in the sample arrangement shown in Fig. 1, which is one of the simplest system for pulse generation. Cellophane diaphragms are used to separate the sample solutions from the electrode solutions; sample solution II is a gel solution of sodium chloride containing agar. Ion-exchange membranes used are Selemion CMG-10 (cation-selective) and AMG-10 (anion-selective) manufactured by Asahi Glass Co., Ltd.

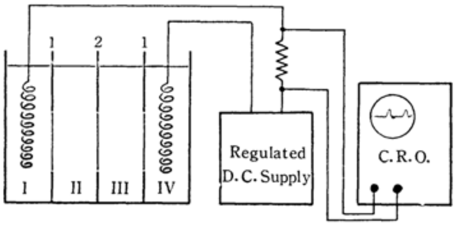

Fig. 1. The sample arrangement for observation of anomalous conduction and the measuring apparatus.
1. Cellophane (Visking) diaphragms
2. Ion-exchange membranes
Electrode solutions I and IV and sample solution III are 0.05 N NaCl solutions and sample solution II is 0.05 N NaCl solution containing agar (1.5 wt%).

The relationship between the voltage applied and the current passed is ohmic at the initial state when the voltage is applied. But, when the membrane is cation-selective and the electrode I is positive, the current decreases with time and reaches a constant value, which is characteristic of the system and independent of the voltage applied. When the polarity of electrode is reversed, such a decrease is not observed.

When higher voltages are applied to the system in the former case, the current no longer decreases and repeated pulses superimposed on the direct current are observed, an example of which is shown in Fig. 2.

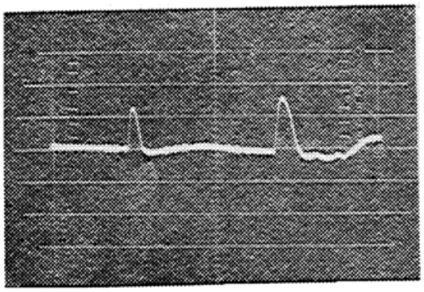

Fig. 2. The pulse train superimposed on the direct current across the ion-exchange membrane in Fig. 1.

The following mechanism is proposed for this anomalous conduction. When the current passes across ion-exchange membranes, the concentration polarization takes place in the diffusion layers (interfaces between solutions and membranes), owing to the difference of transport numbers of ions in the solution and membrane phases. When the limiting current flows, the salt concentration in the salt-depletion diffusion layer, which is built up facing to the anode in the case of cation-selective membranes, becomes zero[3]. When a higher voltage than the critical one is applied to the system, a higher current governed by the ohmic resistance of the system passes initially but, as soon as the salt-depletion layer is built up, a lower and stationary diffusion-controlled current is observed. In this stationary state, the current is independent of the voltage applied, and the electrical potential difference at the salt-depletion layer increases remarkably with the increase of the applied voltage.

When the electrical potential difference becomes higher than a critical value, a sudden increase in current is observed probably because the increasing dissociation of water occurs in the salt-depletion layer. However, such a high current can not pass stationarily, because the salt-depletion layer is built up again in the cource of time. Thus the current passing through this system oscillates along the limit cycle on the voltage-current diagram of the diffusion layer, which is shown in Fig. 3. At the point A the increasing dissociation of water occurs, and the point B is determined by

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1) C. Forgacs, *Nature*, **190**, 339 (1961).

2) K. Yamamoto, *Kagaku*, **31**, 265 (1961).

3) T. R. E. Kressman and F. L. Tye, *Discussion Faraday Soc.*, **21**, 185 (1956); N. W. Rosenberg and C. E. Tirrell, *Ind. Eng. Chem.*, **49**, 780 (1957).

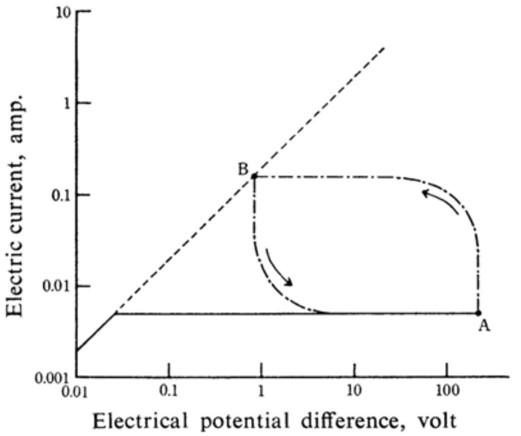

Fig. 3. Log-log plot of electric current against electrical potential difference at the salt-depletion diffusion layer.

the ohmic resistance of the system.

When an aqueous sodium chloride solution is used as the sample solution II, the stationary diffusion-controlled current is not established and the pulse current is not observed. The gel-like structure of agar stabilises mechanically the diffusion layer. Concentrated glycerol-water solutions of sodium chloride can beused as the sample solution for pulse generation.

The same behavior is observed in a double ion-selective membrane, which is made by pressing cation- and anion-selective membranes face to face. In this case, a junction plane between two parts of the membrane plays the same role as the salt-depletion diffusion layer in the case of the single-membrane system.

The rectification effect is also observed in these cases. Further extensive investigations are being made in order to exploire the electric circuit elements with ions as charge carriers and examine its similarity with biological membranes.

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