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Electrochemical Properties of the Ion-Exchange Membranes Junction. II.*

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Current flow through the membranes rectifying system in the reverse direction depends mostly on the potential difference built up between the membranes. The change of the potential difference between membranes during the current flow in the reverse direction is significantly greater than, and of the opposite sign from, that in the forward direction. The current in the reverse state is higher than expected because of imperfect experimental conditions (impurities in the system) but it is still sufficiently small compared to the current in the forward state. Besides, the effect of rectification is lower than expected because of the sluggishness of the system during the fast transition from the forward into the reverse state.

Electrolytical rectifying systems constructed by means of ion-exchange membranes have been known for several years[1,2,3]. The mechanism of rectification of alternating current in such systems has not yet been investigated intensively. The purpose of this series of papers is to throw more light upon the phenomena causing the rectification of alternating current in such membrane systems.

A previous paper[3] reported on the phenomena at the membranes junction of a carefully selected system, and on the behaviour of such a system during the flow of current in the forward direction. The purpose of this paper is an investigation and analysis of the behaviour of the same system during and after the flow of current in the reverse direction and its behaviour during the application of alternating voltage.

EXPERIMENTAL

The rectifying device resembles the one previously described.[3]

The system was first polarized by means of single pulses of constant current but in the reverse direction, *i.e.* the negative terminal of the current source was connected to the cation-exchange membrane side of the system. Because of a relatively high resistance of the investigated system in the reverse direction a higher resistor (10 Mohm) for current stabilization had to be built into the current circuit. Special conditions of the experiment necessitated the use of a direct current amplifier with a very short rise-time[4].

Besides the measurements with a single pulse of constant current the rectifying system was polarized by single pulses of constant voltage, in which case the

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technique used was in no way different from the one used in measurements with constant currents.

In addition to investigations with single pulses, alternating voltages of different frequencies were applied on the rectifying system. The sources of alternating voltage used were sinusoidal and square wave a. c. generators. The ensuing responses were registered on a cathode rays oscilloscope (CRO) screen.

RESULTS

A constant current pulse in the reverse direction gives on the CRO screen the characteristic dependence of voltage on time (Fig. 1). The change of voltage during the flow of a pulse is relatively high in the current range applied (up to 4 μA). With such small currents it means that the overall apparent resistance of the system to the flow of current in the reverse direction, is high. Table I. shows the characteristic results:

TABLE I

I (μA)	0.47	0.74	1.14	1.37	1.93	2.57	3.24	3.90
E (mV)	146	217	346	420	561	760	938	1176
R_a (kΩ)	312	293	303	307	291	296	289	302

Following the termination of a pulse the voltage drop does not consist of two parts, as was the case in the investigation of the system in the

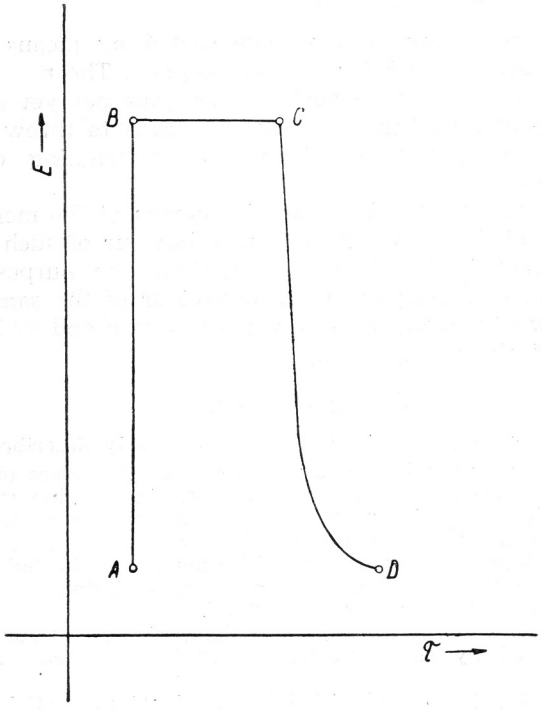

Fig. 1. Characteristic time dependence of the voltage during a constant current pulse in the reverse direction.

forward direction. The voltage drop has no sharp part at all. It decreases with time exponentially and rather rapidly to the starting value. This starting value of voltage is reached in 5 to 7 msecs. after the termination of the pulse. Apparently the rate of the drop does not depend practically on either the current used or the length of the pulse.

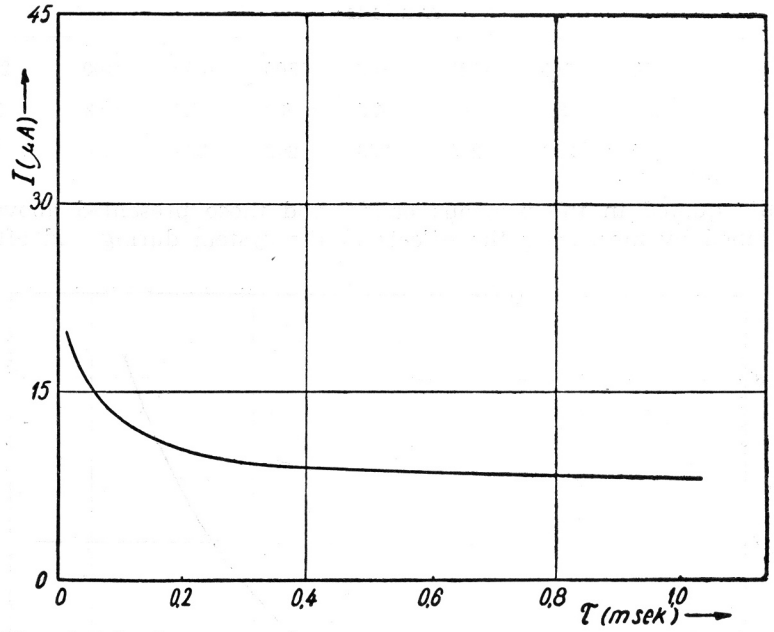

Fig. 2. Characteristic time dependence of the reverse current during a constant voltage pulse of 20 msecs. duration.

A constant voltage pulse of approximately 20 msecs duration in the reverse direction gives on the CRO screen the characteristic time dependence of reverse current flow through the system. (Fig. 2). It is evident that current flow through the system following the switching on of a pulse drops within approximately 0.4 msecs to a small and apparently stable value. This »stable« value of current depends on the voltage used and increases with it as shown in Fig. 3. But if a constant voltage is forced upon the system in the reverse direction for a longer period of time (10 minutes) it becomes apparent that the »stable« value for current from Fig. 2 keeps changing for some time. The current continues to fall, and the rate of decrease lessens with time (Fig. 4). It is interesting to note that after a longer electrolysis it takes a certain time for the system to return to its original state. This has been tested by sending short pulses (approx. 20 msecs.) of constant voltage through the system at determined intervals following the termination of a ten-minute electrolysis. Changes of »stable« values of current were observed on the CRO screen. These values for »stable« current are plotted against time elapsed after the termination of the ten-minute electrolysis in Fig. 5. In the period immediately following the termination of a ten-minute electrolysis these values are smaller, and with time they tend to approach the initial values for current before electrolysis.

The dependence of »stable« current on the voltage used during the application of short (20 msecs.) pulses yields again values for the overall apparent resistance of the system. Variations are very small at lower voltages, and above 1400 mV values of the overall apparent resistance of the system begin to decrease. For results see Table II.

TABLE II

E (mV)	600	900	1100	1300	1500	1800	2100	2500
I (μA)	2.1	3.2	3.9	4.5	6.2	7.7	10.2	14.4
R_a (kΩ)	286	282	285	289	242	234	206	174

Results quoted in the previous paper[3] and those presented above have been obtained by measuring the effects in the system during and after the

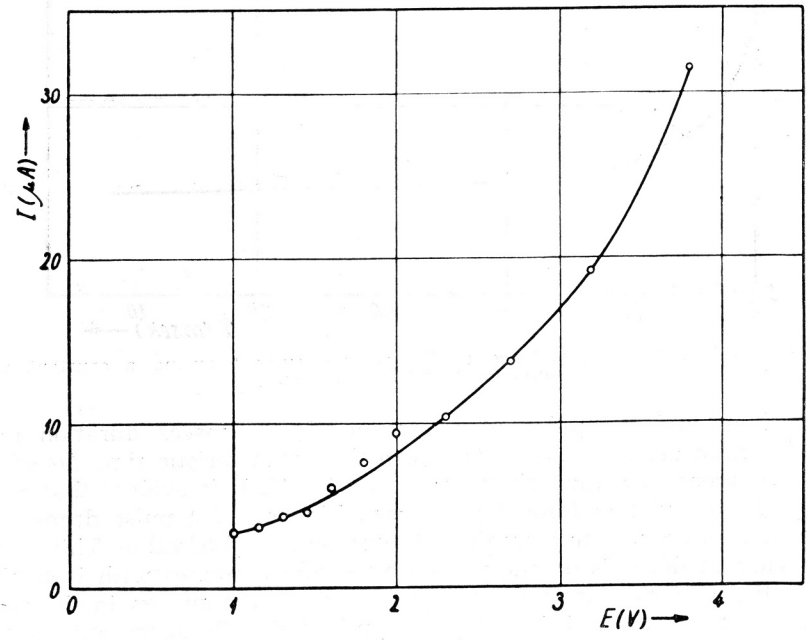

Fig. 3. »Stable« reverse current as a function of the applied voltage.

flow of a *single* electric pulse in the forward or in the reverse direction. The following results contained in Figs. 6, 7, and 8, on the other hand, represent measurements carried out in the system during the application of *alternating voltage*. Fig. 6 shows a characteristic form of a wave of sinusoidal or square alternating current after its flow through the tested system. The assymetry of the form of the wave is easily noticed in both cases.

Measurements, of the dependence of rectification of a. c. on the frequency used has given very interesting results. It has been noticed that the effect of rectification decreases with an increasing frequency, and above a certain frequency it completely disappears. Fig. 7 shows changes in the form of the

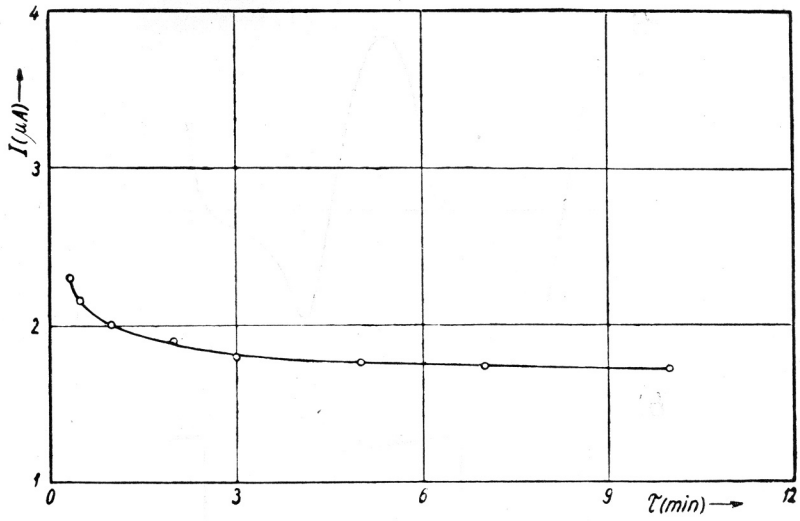

Fig. 4. Typical time dependence of the reverse current during the ten-minute electrolysis.

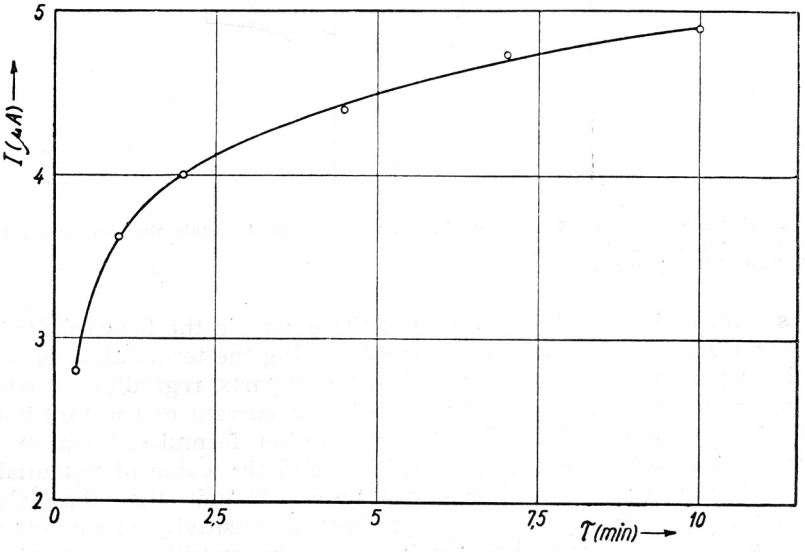

Fig. 5. »Stable« reverse current versus time passed after the termination of the ten-minute electrolysis.

wave of sinusoidal a.c. through the investigated system in dependence on the frequency of current used. Identical measurements, but with square a.c. and use of a smaller range of frequency, are represented in Fig. 8.

DISCUSSION

1. *The rectifying System During the Reverse Current Flow*

The investigation of the behaviour of a rectifying device during the flow of current in the reverse direction has yielded results somewhat different

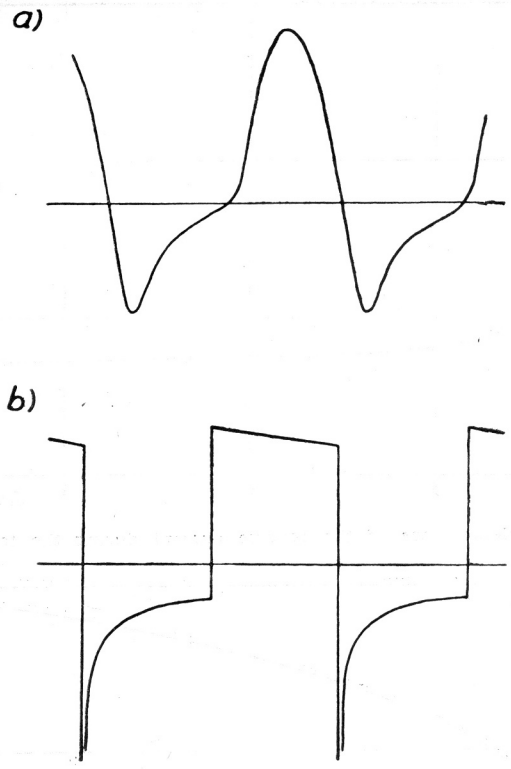

Fig. 6. Typical wave form of the alternating current flow through the rectifying device:
a. with the sinusoidal a.c.
b. with the square a.c.

from those obtained in the investigation of the device in the forward direction. In the former case the decrease in voltage following the termination of a pulse has no sharp part, nor can it be divided into two parts, regardless of whether the measurements were carried out with constant current or constant voltage. However, if we give credence to the assumption formulated earlier[3] that during the pulse both ohmic drop of voltage and the value of potential difference at the junction can change, we must conclude that the value of immediate voltage drop (IR) is below the limit of sensitivity of the amplifier, and could not be registered. The sensitivity of the amplifier used was such that it could register two points corresponding to a potential difference of 15 to 20 mV's. This means that the sharp voltage drop in current range applied could not be observed if the ohmic resistance in the interface had a value somewhere between 10^3 and 10^4 ohms at the end of a pulse. With the resistance in the interface having been earlier[3] determined at approximately 5.5×10^3 ohms, the result obtained indicates that there is no essential change of this value during the pulse. This means that the ohmic resistance of the interface in the reverse direction constitues a negligible obstruction to the current flow through the system. But as the results indicate that the overall apparent resistance of the system in the reverse direction is quite

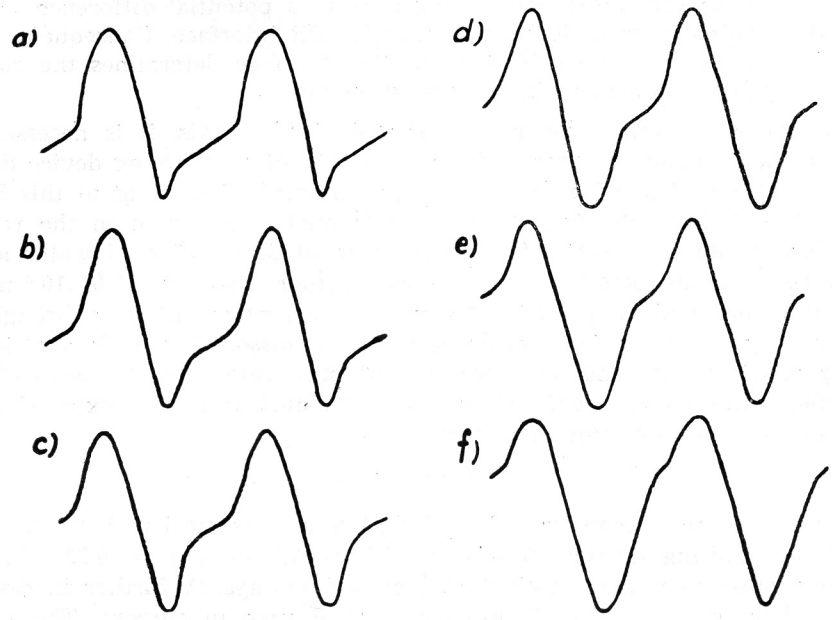

Fig. 7. Wave form of the sinusoidal a.c. through the rectifier as a function of the frequency:
a. 50 c/s d. 2000 c/s
b. 200 c/s e. 8000 c/s
c. 500 c/s f. 15000 c/s

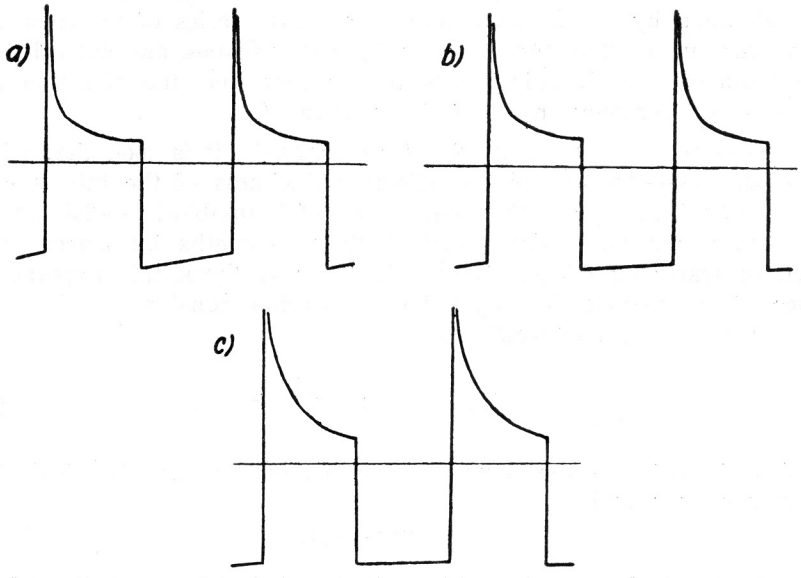

Fig. 8. Wave form of the square a.c. through the rectifier as a function of the frequency:
a. 94.5 c/s
b. 310 c/s
c. 1052 c/s

large, it can be concluded that during a pulse a potential difference greater than the original is established at the ROH || HR interface. Consequently, the variation of the potential difference at the interface determines the current flow through the system in the reverse direction.

In order to explain the rest of the obtained results, it is necessary to analyse the hypothesis[1] regarding the behaviour of a rectifying device during the application of a pulse in the reverse direction. According to this hypothesis, the limiting steady state current through the system in the reverse direction should be determined by the rate of dissociation of water at the interface, this rate being, as it is known[2], rather small ($k = 2.6 \times 10^{-5}$ min^{-1}). Therefore the maximal possible steady state current would flow through the system only if all the ions resulting from the dissociation took part in the transport of current and none recombined into water. On the basis of this hypothesis the limiting current can be calculated from the expression for the rate of the dissociation of water*:

$$v = k_{diss} \cdot c_{H_2O} \qquad (1)$$

Assuming that the dimensions of the interface are identical with the previous ones[3] the limiting current thus obtained would amount to 0.22 μA. This limiting value should be reached at a certain voltage. A further increase of voltage beyond that value should cause no change in current. The results show that the behaviour of the rectifying device during the application of a pulse of constant voltage in reverse direction meets apparently the original expectations. In the first moment a larger current flows through the system, but very soon it decreases to a certain low »stable« value. »Stable« values of current obtained by the measurement of a whole series of voltages applied are, however, higher than the theoretical limiting values, and even dependent on the voltage applied. This points to the fact that the situation in the system is more complex than originally assumed.

In analysing the conditions of the experiments, it is seen that with the voltages used (1 — 2.5 V) and the effective thickness of the interface being 10^{-4} cm, the field strength at the interface amounts to about $1 - 2.5 \times 10^4$ V/cm. It is possible that an electric field of these strengths influences the dissociation of water (2nd Wien effect). In order to check this hypothesis the influence of the electric field upon the dissociation constant has been calculated from the known expression[6]:

$$\frac{K(x)}{K(o)} = 1 + \bar{b} + \frac{\bar{b}^2}{3} + \frac{\bar{b}^3}{18} + \ldots . \qquad (2)$$

K(x) and K(o) are the dissociation constants in the electrical field x and o, respectively, and

$$\bar{b} = 9.695\ (v/DT^2)$$

where v is the field strength in V/cm, D the dielectric constant, and T the absolute temperature.

* k_{diss} is chosen as the best available approximation.

The ratio K(x)/K(o) thus obtained at the field strength 2.5×10^4 V/cm is 1.035, which means that the dissociation has increased with the field strengths used. This increase is, however, very small and the number of ions that come into being under the circumstances does not justify the observed higher currents.

Another circumstance to be taken into account, while trying to explain the observed phenomena, is the fact that the system is not ideally free of impurities. The ionic exchange membranes were transformed into an H^+ and OH^- form by the action of 1 *N* H_2SO_4 and 1 *N* NaOH, then washed and kept in redistilled water, not in an inert atmosphere but exposed to the air. Therefore it is very likely that they are polluted, mainly by CO_2 from the air. Besides, a small quantity of foreign ions left over from the transformation of the membranes into the H^+ or OH^- form could be present. The evidence of the experiment (Fig. 4.) in which the system was subjected to a ten-minute electrolysis strongly supports the supposition that impurities were present. The decrease of current under the circumstances indicates a reduction in the number of conductive particles, ions, at the interface. This means that impurities present in the beginning of the electrolysis are slowly extracted from the interface. When the source of constant voltage is switched off these impurities penetrate back into the interface, and the device becomes more conductive again (Fig. 5).

Actually the constant value of current flow through the system in the reverse direction after the purification of the device by electrolysis is still considerably higher than the theoretically calculated limiting currents. This could be the result of the presence of carbonic acid whose rate of dissociation may be greater than the rate of dissociation of water. Lacking data on the rate of dissociation of carbonic acid this influence could not have been numerically evaluated.

And finally there could be the impurities in the tested system that could not be extracted from the interface by electrolysis. If a very small quantity of SO_4^{2-} remained in the cation-exchange membrane after its transformation into an H^+ form, and a very small quantity of Na^+ in the anion-exchange membrane, then these ions during the electric pulse applied in the reverse direction penetrate the interface, which means that they can increase the overall current. With currents of the reverse direction which are generally very small as compared to those in the forward direction, this effect can become appreciable.

From our results and this analysis it follows that the limiting steady state current, determined by the rate of dissociation of water, is not reached in the tested system. Consequently the currents obtained during the pulse in the reverse direction are determined, as it is stated above, by the value of the potential difference between the membranes.

2. *The Mechanism of Rectification*

The results quoted above can give a more detailed picture of the mechanism of rectification in the tested system. The main characteristics of the mechanism of the rectification of a. c. have been conceived by Lovreček, Despić and Bockris[1]. They assume that in the forward direction movable ions under the influence of the electric field are impelled toward one another

and react at the junction: current flows without much difficulty. In the reverse direction current is also transported by movable counter-ions, but now away from the junction. These ions, however, are the product of dissociation of water at the interface and the area surrounding it: a relatively slow process. Therefore this current is small compared to the current in the forward direction. Consequently the system is not equally conductive in both directions or, in other words, it rectifies the current.

The results of the previous[3] and present investigations indicate more precisely the causes of the rectification of a. c. During the flow of current through the system in the forward direction two processes take place: a change in the ohmic voltage drop (IR) in the water layer between the membranes, and a variation of the potential difference between them. Both effects are of the same magnitude and therefore have an approximately equal influence upon the apparent overall resistance of the system, *i.e.* upon the current flow through it. In the reverse direction, however, the change in the potential difference between the membranes is considerably larger than the change in the ohmic voltage drop in the interface. Therefore this change regulates the overall apparent resistance of the system in the reverse direction. In its absolute magnitude it is considerably greater and of the opposite direction than the change in the potential difference between the membranes in the forward direction. Thanks to this, the apparent overall resistance of the system in the reverse direction is considerably greater than the apparent overall resistance of the system in the forward direction. This means that the current flow through the system in the reverse direction is considerably smaller than in the forward direction. (Fig. 6).

The sluggishness of the system influences the effect of rectification. It manifests itself in the fact that the rectifying system does not return to its original state immediately after the termination of a pulse in the forward direction. As has already been said[3] the areas closest to the active part of the rectifying system then contain a larger concentration of movable ions than in the stage immediately preceding the pulse. In the moment of change of polarity of the current source this excess of movable ions is extracted from these areas by the action of the electric field. This means an increase in current in the reverse half-period and a lowering of the effect of rectification of a.c.

Measurements of the dependence of rectification upon the frequency of a.c. used confirm the described lowering of the rectifying action of the system. It follows from Figs. 7 and 8 that an increase of frequency evidently lowers the effect of rectification. At low frequencies the time necessary for the pulling out of previously injected movable ions is small compared to the duration of a reverse half-period, and the current relatively quickly drops to a low level. The average current in the whole of a reverse half-period is small: rectification is good. At higher frequencies approximately the same quantity of previously injected ions is pulled out of the system while in the reverse state. Therefore the current drops with time in a way similar to that before, however, the length of the reverse half-period is smaller. Therefore the average value of current is greater, which means that the system is more conductive, *i.e.* the rectification is poorer.

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IZVOD

Elektrokemijska svojstva kontakta ionsko-izmjenjivačkih membrana. II.

B. Kunst i B. Lovreček

Jakost struje, koja prolazi kroz membranski ispravljački sistem u zapornom smjeru, ovisi uglavnom o potencijalnoj razlici na dodirnoj površini dviju membrana. Promjena te potencijalne razlike za vrijeme prolaza struje u zapornom smjeru znatno je veća i suprotnoga predznaka od odgovarajuće promjene za vrijeme prolaza struje u propusnom smjeru. Jakost struje, koja prolazi kroz sistem u zapornom smjeru veća je od očekivane zbog neidealnih uvjeta rada (prisutne nečistoće u sistemu), ali je još uvijek dovoljno malena, da omogućuje dobar ispravljački efekt. Efekt ispravljanja u ispitivanom sistemu manji je od očekivanog i zbog pojave tromosti sistema kod brzoga prijelaza iz propusnog u zaporno stanje.

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