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A Hydrogen-Oxygen Fuel Cell using an Ion-exchange Membrane as an Electrolyte

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RESUME. — Des densités de courant de l'ordre de 100 mA/cm² sous 0,6 volts ont été obtenues avec des piles utilisant des membranes échangeuses d'ions cationiques lavées à l'eau; il a été montré que l'élimination de l'eau produite limite considérablement le rendement de la pile. Des piles à membrane anionique produisent des densités de courant beaucoup plus faibles. Une tentative d'explication en a été faite en se basant sur des mesures d'impédance.

SAMENVATTING. — Stroomintensiteiten van de orde van 100 mA/cm² onder een spanning van 0,6 volt werden bekomen met brandstofcellen die gebruik maakten van kationische ionenuitwisselaarmembranen die met water gewassen werden; men heeft bewezen dat de verwijdering van het geproduceerde water, het rendement aanzienlijk beperkte. Brandstofcellen met anionische membranen brengen een belangrijk zwakkere intensiteit voort. Men heeft, gesteund op impedantie metingen, getracht hiervan een verklaring te vinden.

SUMMARY. — Using an acidic type of water leached ion exchange membrane, cell current outputs of the order of 100 mA . cm^{-2} at 0,6 V cell voltage have been obtained; the removal of produced water largely limits the cell performance. Cells using the alkaline type of membrane exhibit much smaller current densities, which was demonstrated to be caused by the hydrogen electrode. A tentative explanation is offered on the basis of impedance-measurements.

ZUSAMMENFASSUNG. — Stromdichten in der Grössenordnung von 100 mA/cm² bis 0,6 V wurden mit Brennstoffzellen, welche mit Wasser gewaschene Kationenaustauschermembranen enthielten, erreicht; es wurde gezeigt, dass die Entfernung des gebildeten Wassers die Ausbeute der Brennstoffzelle beträchtlich begrenzt. Brennstoffzellen mit Anionenaustauschermembranen produzieren wesentlich niedrigere Stromdichten. Ein Versuch zur Erklärung auf der Basis von Impedanzmessungen wurde gemacht.

Introduction.

Since about 1956 a number of ion exchange membrane fuel cells has been described in the literature [1]. Some of them have been brought to an advanced stage of development [2, 4, 13].

The organization TNO has developed ion exchange membranes in the late fifties [6], and much fundamental work has been done in this field [7].

It seemed worth-while to investigate whether these membranes could be applied in a membrane fuel cell.

In some membrane fuel cells that have been investigated by others, membranes are used containing excess electrolyte. In most cases this is done to improve the discharge performance [1h], sometimes as a consequence of a special design [1d]. Some type of membranes split off electrolyte because of chemical instability [3].

From the beginning, however, we decided to restrict our study to fuel cells with membranes in the completely leached form, i.e. without any excess electrolyte. Such membranes can be obtained by rinsing thoroughly with pure water. After the membranes have been brought in the appropriate acidic or alkaline form.

It is useful to see in what aspects the ion exchange membrane fuel cell differs from other low temperature fuel cells. We shall limit ourselves to a few crucial points.

A fuel cell using a liquid electrolyte contains a gas-diffusion-electrode of more or less complicated structure as an essential part. This gasdiffusion-electrode has to meet several requirements to allow a good operation. Many of these requirements can be dropped in a membrane fuel cell, the electrode generally consisting of

a thin layer of an active electro-catalyst deposited on the membrane.

The membrane can be considered in a certain sense as a solid. This means that the true electrode surface is restricted to that area where the catalyst particles and the membrane material meet. In this connection one can ask whether the true membrane-electrode can be considered as a porous electrode in the modern sense [8]. Our experiments indicate that this is not the case, but it must be added that this may be valid only for our method of preparing the membrane-electrodes.

Another consequence of the peculiar structure of the membrane arises in connection with the production of water. Unlike other fuel cells, the product water cannot be absorbed in the electrolyte in order to evaporate it outside the cell, since it will be expelled in liquid form from the membrane as long as the water-content has its maximum value. Therefore, the product water has to be removed by evaporation from the places where it is formed. In the case of cells with the acidic membrane, the heat available for the evaporation is generated dominantly at the oxygen-electrode as a consequence of irreversible losses. This happens to be the electrode where the product water is formed according to:

$$O_2 + 4\,H^+ + 4\,e \rightarrow 2\,H_2O$$

It may be noted that more water will be liberated than a half mole per Faraday because of the hydration shell of the proton. It has not been proved as yet that electro-osmotic water transport across the membrane contributes to the liberation of water at the oxygen electrode.

Excessive evaporation of water, causing at least a partially dried out membrane has a severe effect on the performance of the cell as will be shown later on. Whether the ohmic resistance, the oxygen over-voltage or the hydrogen over-voltage is the most sensitive to drying out cannot be discussed here. The amount of residual water in the membrane is governed by the shape of the water vapor absorption-isotherm. In cases when this isotherm has a shape which indicates strong susceptibility to drying out, one has to look for other membranes or use a specially designed cell which controls the evaporation of water.

Another difference between a cell with a liquid electrolyte and a cell with a membrane is caused by the poly-electrolyte character of the membrane. As a rule, polymeric ions exhibit surface active properties because of adsorption at interfaces. When adsorption takes place on an electrode, it is influenced by the dc potential of the electrode and, in our case, may be different at the oxygen electrode as compared to the hydrogen electrode. Quite often the rate of adsorption of large surface active molecules or ions is diffusion controlled, causing frequency dispersion of the double layer capacity and the double layer resistance in potential ranges where adsorption occurs [9, 10].

To obtain a clearer insight into the structure of and into the processes occurring at the electrode-ion exchange membrane interface, we decided to investigate its ac behaviour. We measured the impedances of the hydrogen and the oxygen-electrode at equilibrium as a function of frequency. Information on the double layer capacity was obtained, using mercury as the electrode material so eliminating the disturbing influence of electrode reactions in a large range of potentials.

Experimental Details.

The membranes were of the two kinds developed by our organization. They are prepared either by sulphonation of crosslinked polystyrene in a polyethylene matrix or by introduction of quaternary ammonium groups. Anion exchange membranes were equilibrated with sodiumhydroxide solutions, cation exchange membranes with sulphuric acid solutions. After the equilibration, the membranes were washed with destillated water and later with conductivity water until no alkali or acid could be detected in the rinse water. The membranes were allowed to dry in the open air, and a surface treatment was applied to provide a good contact with the catalyst. Platinum black (Drijfhout, Amsterdam BET surface: 15 m^2/g) was used in amounts varying from 3 to 10 mg/cm^2 membrane surface.

The cell was assembled in a perspex housing, consisting of two identical parts each provided with a current collector, the design of which appeared to be highly important.

Hydrogen and oxygen were used from storage bottles without further purification except in the case of the alkaline cell where carbondioxide was removed.

Impedance measurements were made with cells of which one electrode had a small area (about 0.2 cm^2) as compared with the other. The area of the mercury electrode used during double layer capacitance measurements was very small (0.04-0.06 cm^2); the other face of the membrane was covered with platinum black serving as a non-polarizable auxiliary electrode.

Discharge of Hydrogen-Oxygen Cells.

The current-voltage curves obtained with cells containing acidic and alkaline membranes are presented in figure 1 and figure 2 respectively. The dotted curve in figure 1 is the measured curve after correction for

the ohmic resistance of the membrane. The difference in behaviour between the acidic and the alkaline cell is obvious. In the latter cell, the current density tends towards a limiting value of 25-30 mA/cm², a phenomenon not observed in the case of the acidic cell. It appears that the current output of the acidic cell is of the same order of magnitude as with other low temperature fuel cells. We have found that cells containing membranes soaked in sulphuric acid do not give a higher output.

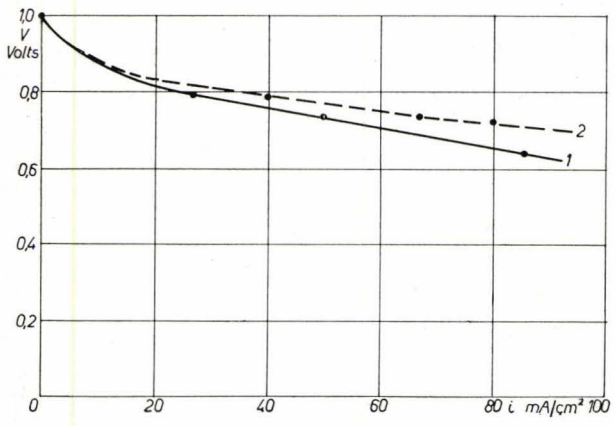

Fig. 1. — Current-voltage curve of the cell : H_2(Pt)/acidic membrane/O_2(Pt).

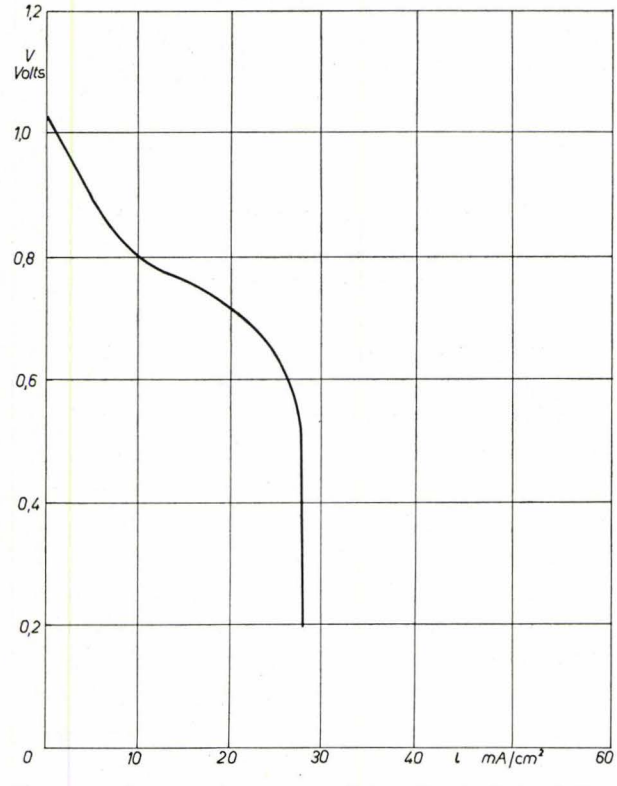

Fig. 2. — Current-voltage curve of the cell : H_2(Pt)/alkaline membrane/O_2(Pt).

Figures 3 and 4 show the influence of the oxygen flow rate on the cell output during discharge over 100 Ω and 3 Ω respectively. The oxygen flow governs the rate of evaporation of the water present at the electrode-membrane interface. It can be seen in figure 4 that both excess and shortage of water have a tremendous effect on the cell output. If the oxygen flow rate is stopped at a point (c) where the cell is dry, the cell voltage increases rapidly, passes a maximum, and decreases, because water collects between the catalyst particles. The water vapour absorption-isotherm, depicted in figure 5, confirms the sensitivity of the membrane to variations of the relative humidity.

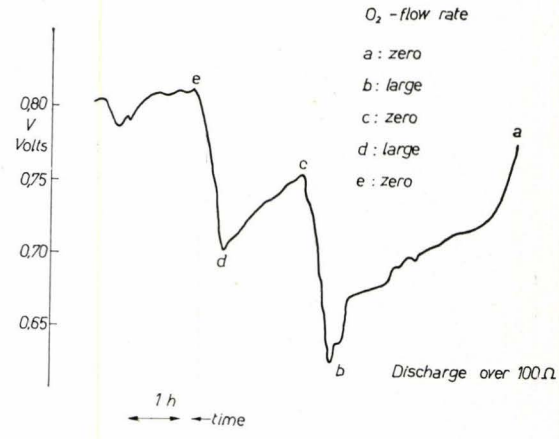

Fig. 3. — Influence of the oxygen flow rate upon the cell voltage; discharge over 100 Ω.

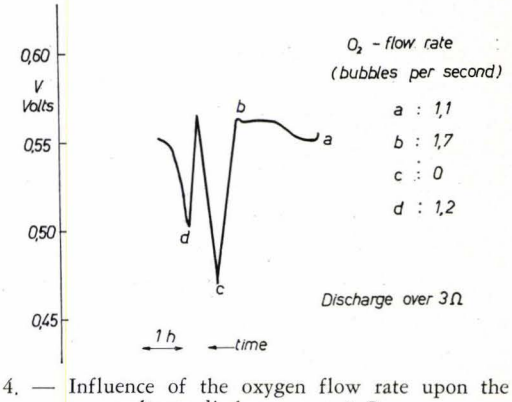

Fig. 4. — Influence of the oxygen flow rate upon the cell voltage; discharge over 3 Ω.

Double Layer Capacitance Measurements.

The capacitance, C_s, is presented in figure 9 as a function of dc potential *) of a mercury electrode in contact with an alkaline membrane. The corresponding data for a mercury electrode in contact with an

(*) Potentials are referred to a hydrogen electrode in contact with the same membrane.

acidic membrane are shown in figure 10. In both cases the frequency was 75 Hz. The frequency dispersion of C_s and the resistance, R_s, is given in figure 11 for the alkaline membrane at dc potentials of + 300 mV and — 500 mV. It is seen that the dispersion depends upon the dc potential.

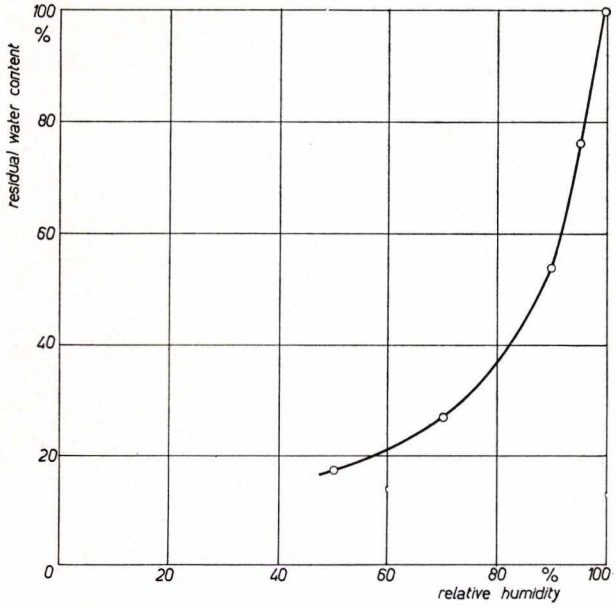

Fig. 5. — Water vapour absorption isotherm at 40°C of the acidic membrane.

As far as we know, systems of this kind, characterized by a very high concentration of surface active polymer chains without a supporting electrolyte have not been investigated before.

We consider the membrane surface of the acidic membrane to consist of polystyrene sulphonic acid chains, which are anchored in the body of the membrane; in the case of the alkaline membrane, the chains are of a polymeric quaternary ammonium type on a polystyrene basis. These chains are present in a high concentration and extend to the electrode surface. Of course, the chains have a certain mobility, which, however, is reduced by their large size; movements over longer distances are limited by crosslinks. It is practically certain that adsorption will occur in a large range of potentials because of the hydrophobic nature of the major part of the chain, especially in the case of alkaline membranes. Moreover, there is no excess of small ions, so that water molecules only can interact competitively with the mercury surface.

In the adsorption of polymeric chain elements there are two possible slow processes which may determine the change of the fractional coverage with frequency: the diffusion of chain elements to the electrode surface and the adsorption process itself. The latter process appears to proceed very fast with mercury *) electrodes. Lorenz and Möckel investigated the adsorption of a variety of organic substances at a mercury electrode and found time constants for the adsorption process of the order of 10^{-5} sec [20] so that slow diffusion plays a dominant role at not too high frequencies [22, 30].

In our opinion, a distinction must be made between the diffusion of chain elements in the immediate vicinity of the electrode surface and the diffusion of the chain as a whole, the greater part of which may be far away from the electrode surface since it is linked to the body of the membrane material. Therefore, only chain elements in the surface layer contribute to a change of the fractional coverage.

Adsorption of chain elements occurs probably by way of « squeezing out », the adsorbed layer being stabilized by Van der Waals forces. Perhaps specific interaction of the mercury with the sulphonic acid groups of the polystyrene sulphonic acid chains must be taken into account. Experiments with N-substituted aniline derivatives [24] suggest that on positive polarization a bonding between the mercury and the π-electrons of the aromatic ring must be considered also, giving rise to a planar orientation. Bulky substituents on the nitrogen atom will not favour this position, however.

Having this picture in mind, the ac behaviour of the mercury-ion exchange membrane interface can be understood. Here we shall not deal extensively with our work in this field, but confine ourselves to a tentative interpretation of the figures. In the case of the acidic membrane (fig. 10), we believe that strong adsorption of polymeric chains exists in the greatest part of the potential range that was covered. At very negative potentials desorption occurs by electrostatic repulsion of the negatively charged chains. The increase of R_s at that range of potentials supports this view. We have not extended the measurements beyond — 1000 mV, because the readings were very unstable there. At a positive potential of about + 300 mV, the structure of the electrical double layer seems to be changed. It is possible that the adsorbed chains change their orientation, because of the increased electrostatic interaction on strong positive polarization. At the positive end mercury is being oxidized as could be observed by the sharp increase of the dc current. In the case of the alkaline membrane (fig. 9), C_s does not change very much with the potential. At strong positive potentials, the mercury is prob-

(*) On platinum, on the contrary, the adsorption rate seems to be much lower, the attainment of adsorption equilibrium of sulphate ions taking about an hour under certain conditions [23].

ably oxidized to mercury oxide while the polymeric chains are desorbed at the same time.

The frequency dispersion of C_s and R_s in principle enables an analysis of the kinetics of the adsorption process *). We treated our data (fig. 11) according to the method of Lorenz and Möckel [20] and found some evidence for a slow diffusion as the rate limiting step in the formation of the electrical double layer. Below 375 Hz, however, the theory [20] is not in agreement with the experimental values.

Impedance Measurements on Hydrogen- and Oxygen Electrodes.

These measurements were performed generally in the frequency range of 3-10,000 Hz. The results will be presented in the complex impedance plane as proposed by Euler [14] and Sluyters [15]. The data of the hydrogen electrode with an acidic membrane and measured at the equilibrium potential at 100% relative humidity are presented in figure 6. The straight line

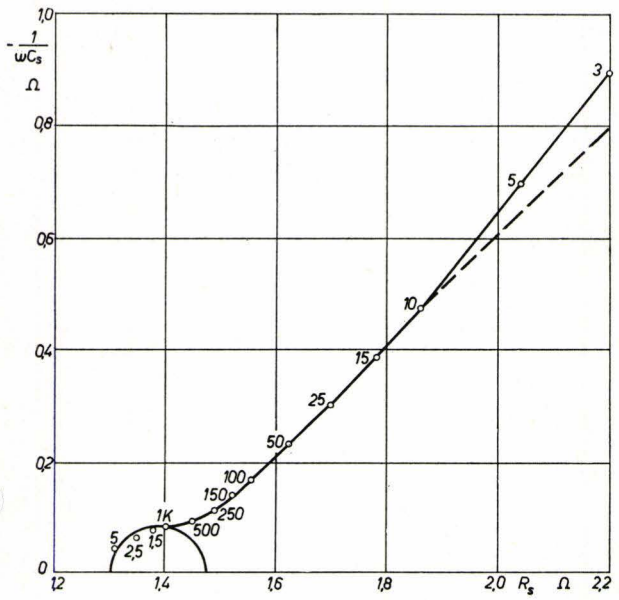

Fig. 6. — Impedance of the hydrogen electrode in contact with the acidic membrane.

with a slope of 45° suggests that the ac behaviour is determined by diffusional effects. At high frequencies, the experimental points deviate from the straight line, probably indicating a charge transfer resistance. From the radius of the semi-circle in figure 6, the exchange current density can be estimated to be 780 mA/cm². The values of the Warburgcoefficient $\sigma = RT/(n^2 F^2 . \sqrt{2} . C \sqrt{D})$, characteristic for a diffusion process, can be found from the frequency dependence of C_s and amounts to $\sigma = 0.78\ \Omega\ cm^2\ sec^{-1/2}$. Herein C is the concentration of the electroactive species and D its diffusion coefficient. The other symbols have their usual meaning. Assuming that we are concerned with diffusion of H_2-molecules in the membrane material, and that $D_{H_2} = 5 . 10^{-5}\ cm^2/sec$ at 20°C [27], the solubility of hydrogen in the membrane is found to be $8 . 10^{-6}$ mole/cm³. This value is appreciably larger than that in water, viz. $0.8 . 10^{-6}$ mole/cm³ [26, 28].

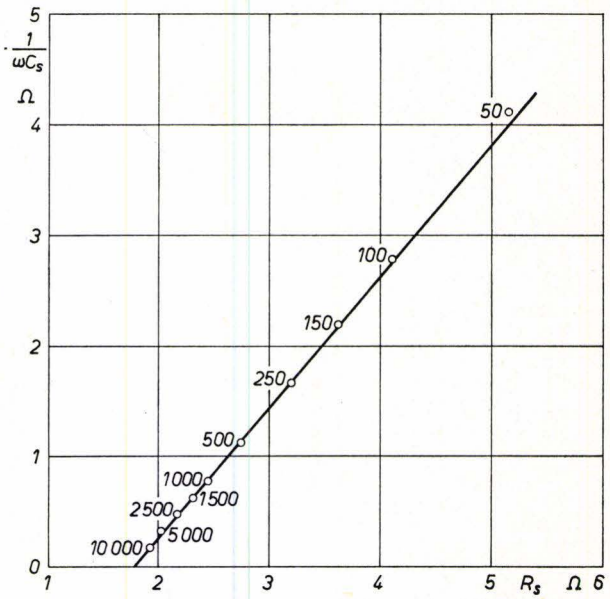

Fig. 7. — Impedance of the oxygen electrode in contact with the acidic membrane.

The upward bending of the curve in figure 6 at very low frequencies may be ascribed to the hydrogen atom adsorption capacitance [16, 17].

The corresponding curve for a freshly prepared oxygen electrode in combination with an acidic membrane, and measured at open circuit potential, is presented in figure 7. Obviously, the rate determining step is a diffusion process, although the slope is somewhat larger than 45°. The value of σ is 13.5 $\Omega\ cm^2\ sec^{-1/2}$ in this case. Assuming $D_{O_2} = 2 . 10^{-5}\ cm^2/sec$ at 20° C [27], the solubility is $2 . 10^{-7}$ mole/cm³, a value smaller than in water, viz. $1.2 . 10^{-6}$ mole/cm³ [28]. We have found that the impedance curve gradually changes towards a circular shape after a few days. This suggests that chain elements are being adsorbed at the electrode thereby hampering the charge transfer reaction concerned. It is clear from figure 7 that below 10,000 Hz no charge transfer resistance is observed. The largest possible value that can be

(*) It should be noted that systems like this may exhibit frequency dispersion for other reasons than those mentioned before. Surface roughness [12] and a non-uniform charge distribution in the membrane surface layer may have similar effects, although the frequency dispersion in these cases is generally not dependent upon the *dc* potential [11]. We assume, therefore, that the observed frequency dispersion is due to the adsorption process.

fitted into the figure amounts to 0.14 Ω cm² (0.7 Ω). This corresponds to a value of the exchange current density of at least 180 mA/cm². This large value contradicts earlier experience on the oxygen electrode (e.g. [25]), and may be connected with the particular structure of the platinum-membrane interface.

The impedance of the hydrogen electrode in combination with the alkaline membrane is presented in figure 8 in the complex plane. On the whole, the

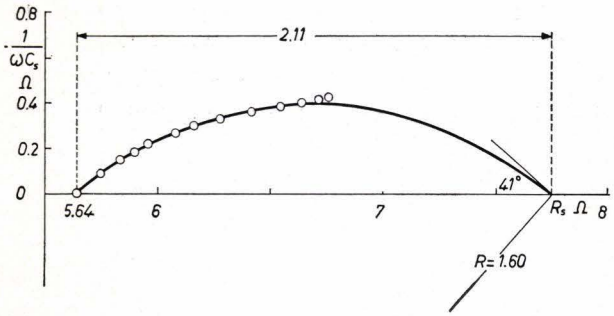

Fig. 8. — Impedance of the hydrogen electrode in contact with the alkaline membrane.

impedance is much larger than the impedance of the hydrogen electrode with an acidic membrane. Although at present we have no reliable data for the oxygen electrode, there are strong indications that the impedance of the hydrogen electrode is also larger than that of the oxygen electrode.

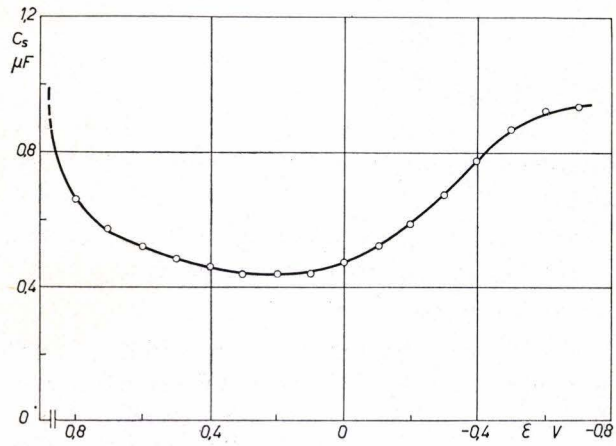

Fig. 9. — Capacitance as a function of d.c. potential of the Hg (area 0.0415 cm²)/alkaline membrane system.

The experimental points in figure 8 coincide practically with a circle, a quarter of which extends above the R_s-axis. A quantitative interpretation can be given on the basis of the assumption that two alternate electrode reactions take place, the first being predominantly diffusion controlled, and the second charge transfer controlled. The Faradaic impedance can then be expressed as:

$$\frac{1}{Z_F} = \frac{1}{r} \frac{1}{\sigma \omega^{-1/2} (1 - j)}$$

where $\sigma \omega^{-1/2} (1 - j)$ is the Warburg impedance of the first electrode reaction ($\sigma = RT/(n^2 F^2 . \sqrt{2} . C \sqrt{D})$, $\omega = 2 \pi f$, f = frequency (Hz), $j = \sqrt{-1}$), and r

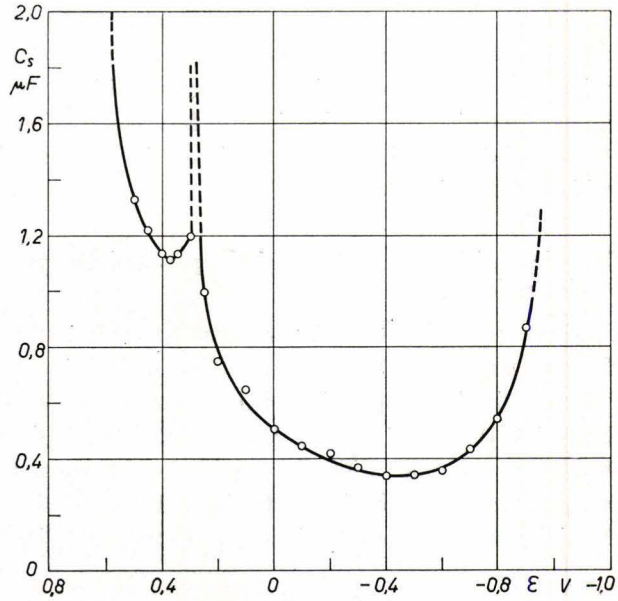

Fig. 10. — Capacitance as a function of d.c. potential of the Hg (area 0.0615 cm²)/acidic membrane system.

is the charge transfer resistance of the second reaction; r and σ can be obtained from the frequency dependence of the components of Z_F. We have found $r = 0.5$

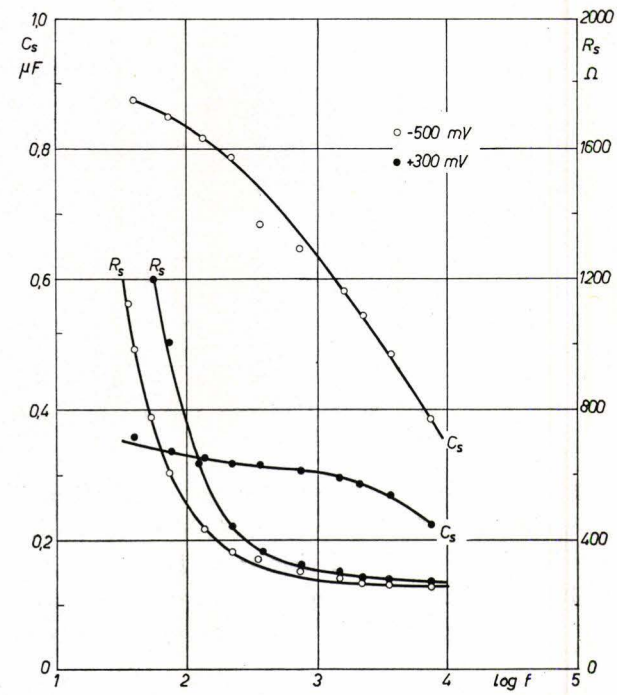

Fig. 11. — Frequency dispersion of R_s and C_s of the Hg (area 0.0415 cm²)/alkaline membrane system.

Ω cm² and $\sigma = 7$ Ω cm² sec$^{-1/2}$. The exchange current density derived from r amounts to 51 mA/cm². If we assume that σ should be associated with diffusion of

hydrogen molecules, the solubility of hydrogen in the membrane material, choosing a value of $D_{H_2} = 5 \cdot 10^{-5}$ cm²/sec [27] can be calculated to be $0.9 \cdot 10^{-6}$ mole/cm³. This value practically equals that for pure water [28]. At present we have not yet established with what processes r and σ correspond.

No experimental data are available at the moment for the oxygen electrode in contact with the alkaline membrane, although preliminary measurements suggest, as was mentioned before, that its impedance is smaller than the impedance of the hydrogen electrode with the same membrane.

It is quite possible that the breakdown of the cell-voltage for the alkaline cell (fig. 2) at 25-30 mA/cm² is caused by the poor solubility of hydrogen in the alkaline membrane compared with that in the acidic membrane.

Finally, we would like to remark that some of the interpretations given above are of a rather preliminary nature, neglecting, as they do, the differences between an aqueous electrolyte and an ion-exchange membrane. The problem how existing theories of electrode processes have to be modified in order to account for the particular properties of the membranes, is under study now.

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