

Rate-determining steps in fuel cells with ion exchange membranes

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RESUME. — Il a été montré à l'aide de mesures d'impédance que le courant, à l'électrode à oxygène de piles à combustible H_2-O_2 à membranes échangeuses d'ions, était régi par une réaction de transfert de charges, dans une large gamme de potentiels. La gamme de fréquences utilisée couvrait six décades.

L'influence de la concentration en ions hydrogène sur la vitesse des processus d'électrode a été étudiée en remplaçant dans la membrane une fraction des ions hydrogène par des ions sodium. Des courants limites proportionnels à la concentration en ions hydrogène ont été observés.

SAMENVATTING. — Door impedantiemetingen werd aangetoond dat de stroom bij de zuurstofelektrode van H_2-O_2 brandstofcellen met ionenuitwisselmembraan wordt bepaald door een reactie van overdracht van ladingen en dit over een breed bereik van potentialen. Het bereik der gebruikte frequenties bedroeg zes decaden.

De invloed van de concentratie waterstofionen op de snelheid van het elektrodeproces werd bestudeerd door in de membraan een klein gedeelte der waterstofionen te vervangen door natriumionen. Grensströmen, evenredig met de concentratie waterstofionen, werden waargenomen.

SUMMARY. — It has been shown by impedance measurements that over a large range of potentials the current at the oxygen electrode of hydrogen-oxygen ion exchange membrane fuel cells is controlled by a charge transfer reaction. The frequency range used covered six decades.

The influence of the hydrogen ion concentration on the rate of the electrode processes was studied by replacing part of the hydrogen ions in the membrane by sodium ions. Limiting currents proportional to the hydrogen ion content were observed.

ZUSAMMENFASSUNG. — An Hand von Impedanzmessungen wurde gezeigt, dass der Strom an der Sauerstoffelektrode von Wasserstoff/Sauerstoff-Brennstoffzellen mit Ionenaustauschermembranen über einen weiten Potentialbereich durch eine Ladungsübertragungsreaktion gesteuert wird. Der verwendete Frequenzbereich umfasste sechs Dekaden.

Der Einfluss der Wasserstoffionenkonzentration auf die Geschwindigkeit der Elektrodenprozesse wurde studiert, indem ein Teil der Wasserstoffionen in der Membran durch Natriumionen ersetzt wurde. Grenzströme, die proportional zum Gehalt an Wasserstoffionen waren, wurden beobachtet.

Introduction.

In a previous investigation [1], impedance measurements on hydrogen-oxygen membrane fuel cells have been reported. These measurements were incomplete in two respects: they were performed at the equilibrium potential only, and the frequency range was limited at the lower side to the rather high value of about 3 Hz. Accordingly, the desired information about the processes governing the performance of the cell could not easily be obtained.

In the present paper we describe the results of impedance measurements of membrane cells through which direct current is flowing. Also the frequency range could be extended down to a value of 0.01 Hz. As far as we know, measurements of this kind have not yet been reported for membrane cells.

The membrane which is used in the present investigation is of a type different from the one used in the previous experiments, which was the TNO-C 60 membrane. This membrane suffered severely from deterioration in a working cell. Although the pre-

sent membrane exhibits less degradation, it is still far from ideal in this respect and, as will be seen below, some implications of the membrane degradation on fuel cell behaviour can be clearly demonstrated with this membrane. Now we are touching upon what appears to be one of the major problems to be solved in this field, viz. the improvement of the chemical stability of organic ion exchange membranes under the conditions prevailing in a working cell, which are apparently much more severe than those in the usual applications of these membranes. However, we will not go deeper into this subject, since it clearly is beyond the scope of this paper which is mainly concerned with the more fundamental aspects of our work.

In many investigations of electrode processes, useful information on rate-determining reaction steps, can be obtained by changing the concentrations of the reactants. For membrane cells one would be particularly interested in the influence of the hydrogen ion concentration on the cell performance. However, in leached membranes the hydrogen ion concentration is fixed by the concentration of the fixed negative charges and changing the latter concentration is impossible without introducing changes in the internal structure of the membrane, the effect of which on the electrochemical properties is unknown.

To overcome this difficulty, we varied the hydrogen ion concentration by exchanging part of the hydrogen ions with sodium ions. It must be realized, however, that again the system obtained differs from the normal one in that the sodium ions introduced constitute a kind of « inert electrolyte ». In other words: the effect of variations of the hydrogen ion concentration is studied at constant ionic strength. Nevertheless, from the preliminary experiments to be described in this paper some interesting conclusions may already be drawn.

Experimental part.

General.

All cells used in this investigation, except those to be described in the last section, contained the cation-exchange membrane « AMF-ion » C-310*) in the acid form and leached until free from excess acid. The membrane is practically colourless and has a thickness of about 0.03 cm; the ohmic resistance, measured in the fuel cell with alternating current of

10 kHz or by a square wave method, amounts to 1.5-1.7 Ω cm² in the acid form. The ion-exchange capacity equals 0.42 meq per gram dry. Probably it consists of sulphonated polystyrene-sulphonic acid (about 9 %) in a Kel-F Elastomer matrix. The water content is about 13% on a dry basis.

The electrode material of both electrodes was commercial platinum black **) (about 1 mg/cm²) applied to the membrane surfaces (area: 2 cm² per electrode) as previously reported [2]. The specific surface of this black is not extremely high (about 20 m² per gram). We have shown that it is relatively easy to prepare platinum blacks with any specific surface up to 40 m² per gram, when the reduction of chloroplatinic (IV) acid is carried out with sodiumborohydride [3] as the reducing agent. The concentration of the latter substance and the rate of addition of the former are of primary importance.

The platinum black electrodes were covered with fine platinum gauze of the same area and clamped in a perspex cell container. Hydrogen and oxygen***), used without further purification, reached the electrodes through a current collector, made of Ni-O-Nel****), and consisting of a perforated plate provided with linear ribs, the distance between the ribs being about 0.3 cm.

The rib systems of the opposite current collectors were perpendicular to each other in order to ensure a good electrical contact between gauzes and platinum black.

The experiments were carried out at room temperature, unless otherwise reported. Hydrogen was always humidified to about 100 % relative humidity at the temperature of the cell and passed over the membrane surface very slowly. Oxygen was kept dry generally and was passed along the membrane at such a rate that an optimal and stable performance was obtained. This rate depends on the temperature rise within the cell due to the passage of current, and on the geometry of the cell components.

Electrical measurements.

Impedances of cell F 108, containing an AMF-ion C-310 membrane, were measured as indicated in Fig. 1. The electrode potential was monitored with a pH-meter (Electrofact). Provisions were made for preventing the a.c. current to flow through the d.c.

**) Drijfhout, Amsterdam.

***) Loosco, Amsterdam.

****) Wiggin & Co Ltd. G.B.

*) Manufactured by the American Machine & Foundry Company, Springdale, Connecticut.

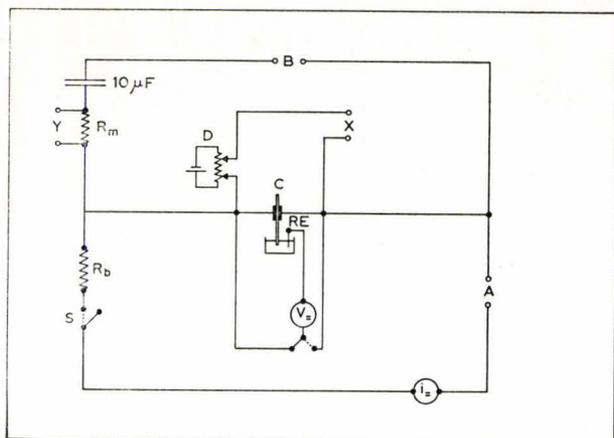


Fig. 1. — Circuit for impedance measurements.

A : d.c. power supply, B : function generator, C : cell, D : dc voltage compensation, RE: reference electrode, R_m : measuring resistance a.c. currents, R: a.c. blocking resistance.

power supply (30 Volts) and the constant d.c. current to flow through the function generator (Hewlett-Packard, Type 3300 A).

For frequencies smaller than 2 Hz the a.c. voltage (less than a few mV) and current were recorded with an X-Y-recorder (Hewlett-Packard, Type 7001 AM) and for higher frequencies with an oscilloscope (Tektronics, Type 502) equipped with a Polaroid camera.

It can easily be shown that an analysis of the ellipse, obtained on the X-Y-instrument, gives the magnitude of the cell impedance Z and its phase angle. Besides, the position of the ellipse with respect to the axes and the direction of rotation provide information to establish the quadrant in which the impedance is located, i.e. the signs of its components. In all cases a positive impedance was observed.

The electrode potentials were measured with reference to a saturated calomel electrode, a piece of the membrane extending from the cell outwards and dipping into a 1 molar HClO_4 solution, which contained the calomel electrode*).

Chemical degradation.

After a certain time of operation, the membrane cells were generally rinsed with de-ionized water, and the residual capacity was determined. Also the acid content of the washing, which in most cases were slightly yellow coloured, was determined by titration.

*) At present this reference electrode has been replaced by a hydrogen electrode in contact with a separate part of the membrane surface, in this way avoiding a possible contamination of the membrane after a prolonged time.

Variation of hydrogen-ion concentration.

Membranes were equilibrated with mixtures of sodiumsulphate and sulphuric acid by shaking overnight. Then membranes were thoroughly rinsed with de-ionized water until free from sulphate ions. The actual hydrogen ion content was determined by equilibrating with excess of a 2 M sodium chloride solution and titration of the acid liberated. The ion exchange isotherm for the AMF-ion C-310 membrane is presented in Fig. 2.

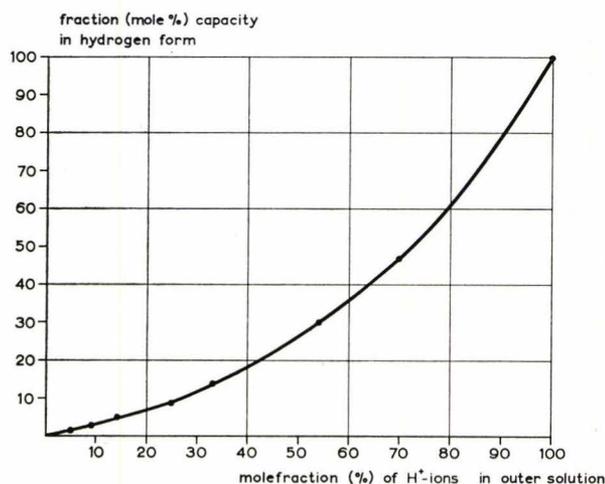


Fig. 2. — Ion exchange isotherm (20°) of the membrane AMF-ion C-310. Outer solution : mixture of 1 normal sodiumsulphate and sulphuric acid.

Results and Discussion.

Impedance measurements.

The results of the impedance measurements with a cell containing an AMF-ion C-310 membrane are presented in Table I. In Figures 3, 4 and 5 complex plane impedance plots are given for the experiments with currents of 0,2 and 100 mA respectively

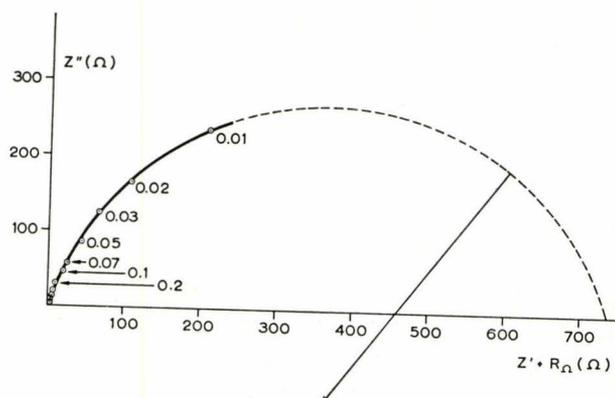


Fig. 3. — Complex impedance of the cell $\text{O}_2(\text{Pt})/\text{C310}/\text{H}_2(\text{Pt})$; $i_- = 0$; $E^{\text{cal}}_{\text{O}_2} = 0.831 \text{ V}$; numbers indicate the frequency (Hz); $R_\Omega = 0.74 \Omega$.

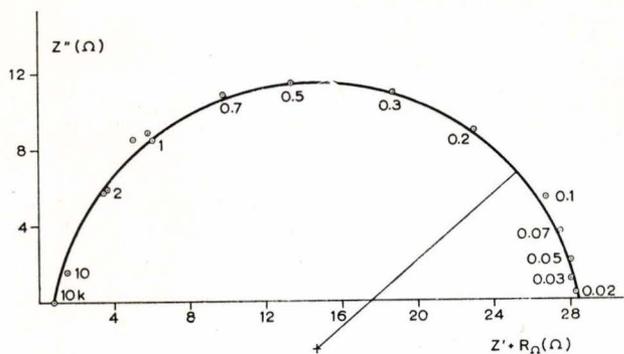


Fig. 4. — Complex impedance of the cell $O_2(Pt)/C310/H_2(Pt)$; $i_- = 2\text{mA}$; $E_{O_2}^{ca1} = 0.717 - 0.695\text{ V}$; numbers indicate the frequency (Hz); $R_\Omega = 0.89\ \Omega$.

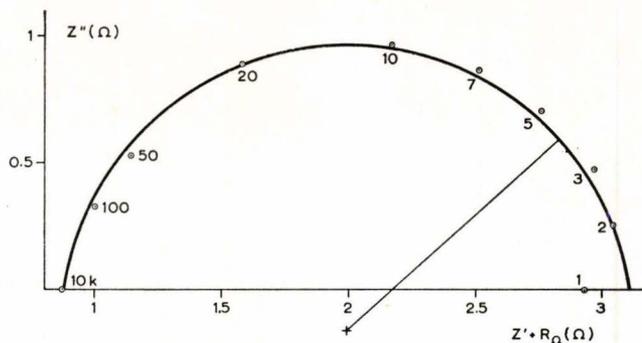


Fig. 5. - Complex impedance of the cell $O_2(Pt)/C310/H_2(Pt)$; $i_- = 100\text{ mA}$; $E_{O_2}^{ca1} = 0.398 - 0.370\text{ V}$; numbers indicate the frequency (Hz); $R_\Omega = 0.87\ \Omega$.

TABLE I

Results of impedance measurements of the cell:
 $O_2(Pt) / C\ 310 / H_2(Pt)$

Number*)	$E_{O_2}^{sce}$ (V)	R_F (Ω)	i_- (mA)**)	$R_F \cdot i_-$ (mV)**)
13	0.831	740	0 (0.04)	0 (30)
6	0.754	336	0.0918 (0.13)	31 (44)
8	0.762-0.790	234	0.092 (0.13)	24 (30)
2	0.737	132	0.21 (0.25)	28 (33)
1	0.654	73	0.55 (0.59)	40 (43)
4	0.634	31.4	1.93	60
3	0.684-0.669	17	1.99	34
9	0.717-0.695	27.6	2.0	55
9***)	0.484-0.485	30	2.0	60
5	0.518-0.513	1.9	47.5	90
7	0.507	2.1	47.5	100
10	0.480-0.471	2.7	47.5	128
11	0.398-0.370	2.24	100	224
12	0.370-0.334	2.72	100	272

*) The numbers indicate the chronological order of the experiments.

***) Figures in parentheses are the values corrected for the extra current carried by the oxygen electrode due to permeation of hydrogen through the membrane.

***) During this measurement the gases hydrogen and oxygen were interchanged. Hence the reported values refer to an electrode different from the one used for the other experiments in the table.

In the following discussion we will neglect the contribution of the impedance of the hydrogen electrode to the total cell impedance. This seems justified in view of the low value of $0.21\ \Omega$ that was found for the impedance of the hydrogen electrode at the equilibrium potential in a cell in which hydrogen had been admitted to both electrodes. Besides, in all experiments with hydrogen-oxygen cells the overpotential of the hydrogen electrode is always negligible compared to that of the oxygen electrode.

The general form of the plots in Figures 3, 4 and 5 resembles the familiar impedance plot [4] of a charge transfer resistance in parallel with a capacitance. However, in our figures the semicircle is reduced to an arc of a circle, the centre of which is shifted to a point below the real axis. This difference can be completely attributed to a different behaviour of the double layer impedance. From Fig. 6, which shows the impedance of a cell in which oxygen is replaced by nitrogen, we infer that the double layer

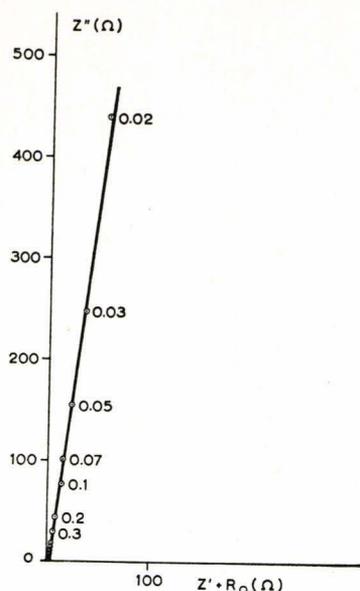


Fig. 6. - Complex impedance of the cell $N_2(Pt)/C310/H_2(Pt)$; $i_- = 0.021$ mA; $E^{anl}_{O_2} = 0.260$ V; numbers indicate the frequency (Hz); $R \Omega = 0.78 \Omega$.

impedance in our case has a phase angle (φ_D) which is independent of frequency but differs from the « ideal » value $\pi/2$. This behaviour is not uncommon with platinum electrodes. [5].

$$R_F = \frac{RT}{nF} \cdot \frac{1}{1 - \alpha} \cdot \frac{1}{i_0 \exp[(1 - \alpha) nF\eta/RT]} = \frac{RT}{nF} \cdot \frac{1}{1 - \alpha} \cdot \frac{1}{i_-} \quad (3)$$

or,

$${}_0E_{O_2} - E_{O_2} = 2.3 \frac{RT}{nF} \cdot \frac{1}{1 - \alpha} \log \left(\frac{RT}{nF i_0} \cdot \frac{1}{1 - \alpha} \right) = 2.3 \frac{RT}{nF} \cdot \frac{1}{1 - \alpha} \log R_F \quad (3a)$$

Therefore, in the frequency range considered, the double layer impedance Z_D can be represented by

$$Z_D = [\omega C_D(\omega)]^{-1} (\cos \varphi_D + j \sin \varphi_D)$$

where $C_D(\omega)$ is the frequency-dependent double layer capacity.

Remembering that the double layer impedance and the faradaic impedance (R_F) are in parallel, it is easy to show that the complex plane plot of the cell impedance, with ohmic resistance omitted, has the shape of an arc of a circle. The radius of the circle $R_F/2 \sin \varphi_D$ and the coordinates of the centre are $(\frac{1}{2} R_F, -\frac{1}{2} R_F \cotan \varphi_D)$. Hence, the value of the charge transfer resistance can be read from the plot as the distance between the intersections of the circle and the real axis, while the ohmic resistance can be found as the intercept on the real axis at the high frequency side of the circle.

In principle the observed shape of the impedance plot could be due to a rate-determining adsorption process as well [6], e.g. the adsorption of oxygen at the electrode. However, the value of the imaginary component of the admittance of the oxygen electrode at a certain frequency should then be larger than the corresponding value in a nitrogen atmosphere at the same frequency. This is not borne out by experiment, however.

The real value of the faradaic impedance down to very low frequencies suggests a negligible contribution of diffusion polarization at the oxygen electrode and hence a current-voltage relationship represented by a Tafel-line

$${}_0E_{O_2} - E_{O_2} = \eta = 2.3 \frac{RT}{nF} \cdot \frac{1}{1 - \alpha} \log (i/i_0) \quad (2)$$

Now, for R_F the relation holds

$$R_F = \left(\frac{\delta \eta}{\delta i} \right)_{i_-}$$

Therefore, making use of Eq. (2)

where the various symbols have their usual meaning.

The relation between overpotential and applied direct current for the experiments of Table I is represented in Fig 7. The best fitting straight line was determined by the method of least squares (the measurements 11, 12 and 13 being left out) and has a slope of 0.114 V.

The analogous representation of the relationship (3a) between overpotential and charge transfer resistance is shown in Fig. 8. The slope of the line has a value of 0.124 V. If α , the transfer coefficient, is taken to be 0.5 and $n = 1$, then according to Eqs. (2) and (3a) the value of the slope of the straight lines should be in both cases,

$$2.3 \frac{RT}{nF} \cdot \frac{1}{1 - \alpha} = 0.115 \text{ V}$$

in satisfactory agreement with the experimental value, which would mean that the rate-determining process

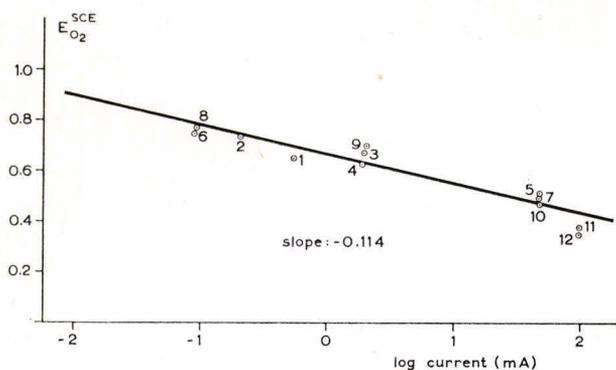


Fig. 7. — Tafel-plot of the measurements of Table I. The straight line was calculated with the least square method; the measurements 11, 12 and 13 not being taken into account.

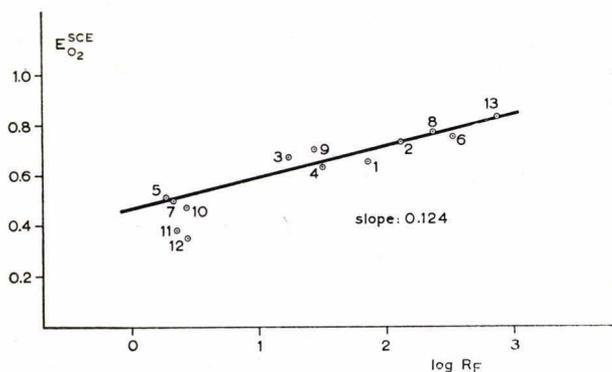


Fig. 8. — Plot of the data of Table I according to eq. 3^a. The straight line was calculated with the least square method; the measurements 11 and 12 not being taken into account.

at the oxygen electrode is a charge transfer reaction in which one electron is involved.

Another check on the applicability of Eq (2) to our experiments, and which gives information about the extent to which each separate experiment of Table I conforms to the picture outlined above, is the value of the product of R_F and i_{∞} , which according to Eq. (3) should be independent of current density :

$$R_F \cdot i_{\infty} = \frac{RT}{nF} \cdot \frac{1}{1 - \alpha}$$

and, for $\alpha = 0.5$ and $n = 1$, would have a value of 50 mV. The resulting figures are shown in the last column of Table I. For the lower current densities a correction has been applied ; it is connected with the permeation of hydrogen gas from the hydrogen electrode through the membrane to the oxygen electrode where the hydrogen will be oxidized by a local cell mechanism. Owing to this process, the oxygen electrode will always carry an extra current proportional to the rate of permeation of hydrogen. This current was found to be about 10 to 25 μ A/cm². In

Table I a value of 20 μ A/cm² was chosen, which corresponds with a current of 0.04 mA.

It is seen that for the lower currents up to 2 mA the values of the product $R_F \cdot i_{\infty}$ scatter around the predicted value of 50 mV in a range between 30 and 60 mV. However for higher currents the value of the product rapidly rises with increasing current density, suggesting the approach to a limiting current. Some indication of the onset of a limiting current can also be seen in the uppermost curve of Fig. 9 (to

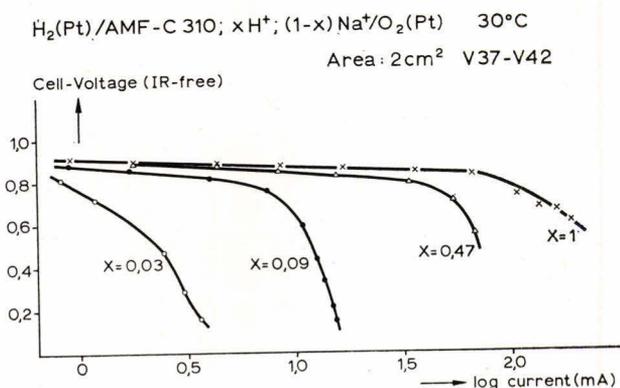


Fig. 9. — Current-voltage curves for cells with different hydrogen-ion concentrations.

be discussed below). Apparently, at high current densities the Tafel equation (2) is no longer applicable, as is also evident from the deviation of experiments nos. 11 and 12 from the straight lines in Figs. 7 and 8. On the contrary the measurements nos. 5, 7 and 10 seem to fit the lines in these figures reasonably well. The discussion of these results is complicated by the phenomenon of membrane degradation which manifests itself particularly clearly in the measurements at higher current densities, as will be seen now.

Inspection of measurements 5, 7 and 10, which were carried out in that order, reveals that in the course of time a gradual deterioration of the cell is taking place. These measurements were carried out with time intervals of 1 resp. 3 days. Measurements 11 and 12 show an analogous behaviour. Obviously the exchange current density decreases in the time. On the other hand, chemical degradation of the membrane material can be observed when the residual ion exchange capacity of the membrane is determined after the cell has been operating for a certain time. In a typical experiment the residual capacity of a membrane C-310, after a service life of approximately 500 hours, was found to be about 46 % of the initial value. The difference was found in the

washings in the form of a water soluble slightly yellow coloured organic acid. Chemical degradation manifests itself in a galvanostatic experiment by a gradual decrease of the value of the oxygen potential. After some time the polarization of the hydrogen electrode, being negligible in the beginning of the experiment, starts to rise. Probably the ion exchange material is degraded by the action of hydrogen peroxide, or some other oxidizing agent which may be formed at an oxygen electrode in acid solution [7], thereby releasing low molecular weight organic sulphonic acid. The anions of this acid will move slowly towards the hydrogen electrode, owing to their small but finite transport number. When arriving there in increasing amounts, adsorption will take place at the hydrogen electrode, so that its polarization will increase.

Effect of the hydrogen ion concentration upon cell performance.

To investigate the influence of the internal acid concentration upon cell performance, we replaced a part of the hydrogen ions in the membrane by sodium ions, as described, and determined the current-voltage curve. The results for various internal hydrogen ion concentrations relative to the total ionic strength at 30° C are presented in Fig. 9. It was verified that the overvoltage of the hydrogen electrode was always negligible. Unfortunately, the accuracy of our measurements does not allow a closer analysis of the straight parts of the current-voltage curves at low current densities. From this figure, it is clear that, even at the highest hydrogen ion concentration, the cell voltage suddenly drops at a certain current density. The effect is very pronounced. We see that with decreasing hydrogen ion concentration in the membrane less current can be sustained. The shape of the curves resembles that of a limiting current. Now, diffusion of oxygen towards the electrode as the current limiting process can be ruled out, since all experiments have been carried out with pure oxygen and it is quite improbable that the solubility of oxygen in a membrane would strongly depend upon its hydrogen ion content. It is more reasonable, therefore, to assume the diffusion of hydrogen ions towards the oxygen electrode to become rate-determining at a certain current density.

The ratio of the limiting current and the hydrogen ion concentration should then be constant. Unfortunately it was not possible to determine the exact values of the limiting currents from the present

results. However, the estimated values in Table II give support to our view.

TABLE II

Mole fraction of capacity in hydrogen form (x)	Limiting current (i_1 , mA)	i_1/x
0.03	4	$0.133 \cdot 10^3$
0.09	16	$0.178 \cdot 10^3$
0.47	94	$0.20 \cdot 10^3$

From the values of the limiting current (i_1) the diffusion coefficient of the hydrogen ion (D_{H^+}) can be calculated. Assuming a constant concentration gradient of the hydrogen ions, C_{H^+} , in the membrane :

$$i_1 = AD_{H^+}F \frac{2 C_{H^+}}{d}$$

in which A is the area of the electrode (2 cm²) and d the membrane thickness (0.03 cm). With $C_{H^+} = x C_0$, where C_0 is the ion exchange capacity in equivalents per cm³ of water ($C_0 = 3.2 \cdot 10^{-3}$ eq/cm³), we find $D_{H^+} = 3 - 4 \cdot 10^{-6}$ cm²/sec. This value is in surprisingly good agreement with the value calculated from the ohmic resistance ($R\Omega$) of the membrane entirely in the hydrogen form ($x = 1$) with the relation

$$D_{H^+} = \frac{RT}{F^2 C_0} \cdot \frac{d}{R}$$

in which use is made of the Nernst-Einstein relationship between diffusion coefficient and electrical mobility.

With $R\Omega = 1.5 \Omega$ cm² we find

$$D_{H^+} = 1.6 \cdot 10^{-6} \text{ cm}^2/\text{sec.}$$

In view of the many simplifications which had to be made, the obtained agreement may be merely fortuitous, however.

Acknowledgement.

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