ELECTROCHEMICAL OXIDATION OF HYDROGEN ON PLATINUM IN THE PRESENCE OF A CATION EXCHANGE MEMBRANE

A. B. Khanin, N. A. Aladzhalova, and N. A. Fedotov

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Polarization curves have been obtained for the ionization of hydrogen on electrodes consisting of platinum clamped to MK-40 and MK-100 membranes. Some features of similarity between membrane-electrode systems and systems with distributed parameters have been noted. It has been established that the generation of current may take place at the surface of the end face or at the lateral surface of the electrode under a film of electrolyte, depending on the properties of the membranes.

In the present work we used MK-40 and MK-100 cation exchange membranes with fixed SO_3^- groups. The former consists of a composition formed from KU-2 ion exchange resin and polyethylene, reinforced with Capron gauze, and the second consists of a sulfonated copolymer of ethylene and styrene. The thickness of the membranes was of the order of 0.5 mm. The preparation of the membranes before the experiment involved treatment with direct current at a density of 15 mA/cm^2 for a period of 15 min in 1 N H_2SO_4 to achieve more complete conversion into the H^+-form, followed by washing for periods of from two days to several months in a large volume of twice-distilled water, which was replaced at intervals, to remove the excess of electrolyte. Even this washing, however, did not give complete removal of electrolyte not absorbed by exchange, and the membranes studied can not be regarded as free from the latter.

The experiments were carried out in a polyethylene cell (Fig. 1), consisting of two sections with a gas chamber, between which the membrane was clamped. The electrodes being studied were clamped against the top of the membrane. The design of the cell ensured efficient contact between the end faces of the electrodes and the membrane. The electrodes studied were prepared from platinum wire with diameter 1 or 2 mm, sealed into glass tubing. The plane polished surface of the end face of the platinum wire was perpendicular to its axis. The auxiliary electrode consisted of platinum gauze clamped to the bottom of the membrane. The pressure of the electrode on the membrane in all cases was equal to 60 kg/cm^2 surface area of the end face of the electrode.

In the measurements it was possible to use two reference electrodes. In an inert atmosphere and for control of the electrode potential in an atmosphere of hydrogen, we used a saturated calomel electrode, connected to short side arms of the membrane which projected outwards from underneath the packing. In an atmosphere of hydrogen one of the two platinum electrodes clamped to the membrane could also be used as reference electrode. The preparation of the electrodes for the experiments involved etching for a period of 3 min in boiling aqua regia followed by boiling in twice-distilled water for a period of 10 min. Hydrogen and argon from cylinders were purified by the usual methods and moistened by passage through twice-distilled water before admission to the cell, to avoid drying of the membrane. The gas was passed into both chambers, and both sides of the membrane were exposed to the same gaseous atmosphere. The assembly made it possible to vary the electrode potential with time at different rates ($\Delta\varphi/\Delta t$) in the range from 75 mV/sec to 0.315 mV/sec.

DISCUSSION OF RESULTS

An extremely important feature for the characterization of the systems studied is the comparatively rapid establishment of the hydrogen potential at the platinum electrode. In the first 3 min after the start of the passage of hydrogen, the potential of the electrode clamped to the cation-exchange membrane is displaced into the hydrogen range and reaches a stable value, with good reproducibility, at a level between −0.28 and −0.30 V with respect to the saturated calomel electrode. If it is assumed that the membrane swollen in water is separated from the surface of the electrode clamped to it by a thin layer of dilute acid, the total measured value of the potential jump should in actual fact include two potential jumps: the first relating to the boundary of separation between

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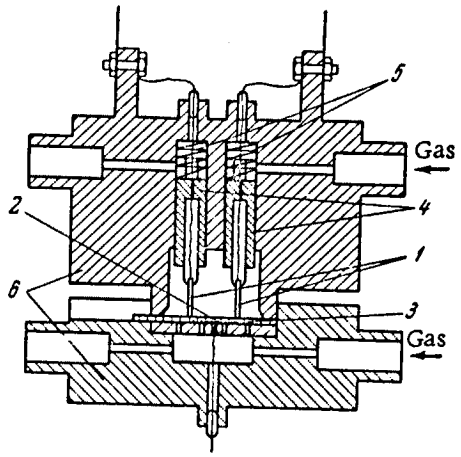


Fig. 1. Polyethylene cell for the measurements: 1) platinum electrodes being studied; 2) auxiliary platinum gauze electrode; 3) membrane; 4) electrode holders; 5) springs; 6) section of cell.

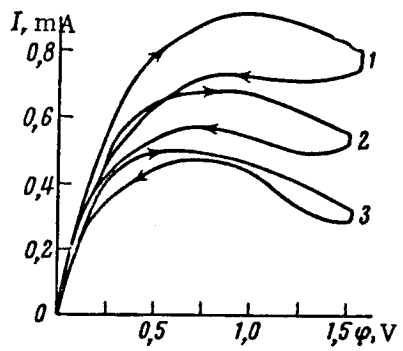


Fig. 2. Polarization curves obtained using MK-40 membrane and a platinum electrode with diameter 2 mm at values of $\Delta\varphi/\Delta t$: 1) 75; 2) 2.6; 3) 0.86 and 0.315 mV/sec. The arrows in this and subsequent figures indicate the direction of the change in potential.

the electrode and the layer of acid, and the second corresponding to the boundary between the layer of acid and the membrane.* The first potential jump at a hydrogen pressure of 1 atm is determined by the activity of the hydrogen ions in the thin layer $\Delta\varphi_1 = (RT/nF) \cdot \ln[a_{H^+layer}]$, and the second, Donnan potential jump is determined by the ratio of the activities of the ions in the layer and in the bulk of the membrane $\Delta\varphi_2 = (RT/nF) \cdot \ln[a_{H^+layer}/a_{H^+membrane}]$. The total measured potential jump is equal to their difference $\Delta\varphi_{meas} = (RT/nF) \cdot \ln[a_{H^+membrane}]$.

From this it follows that the measured value of the potential jump does not depend on the unknown concentration of acid in the layer next to the electrode (the concentration of free acid in the membrane) was estimated approximately by means of pH-paper, and the value found for both types of membrane was of the order of 0.01 N. Analysis of the MK-40 and MK-100 membranes for their sulfur contents gave values of 1.75 and 1.2 N respectively for the hydrogen ion concentrations. Thus the measured potential jump corresponds to the concentration of hydrogen ions in the membrane.

Fig. 2 gives the $I-\varphi$ curves obtained at different values of $\Delta\varphi/\Delta t$ for an electrode with length 5 mm and diameter 2 mm, clamped to an MK-40 membrane, with hydrogen passed through the cell. Each curve was obtained after preliminary activation of the electrode by anodic-cathodic impulses [1, 2], at from $\varphi = 0$ V to $\varphi = 1.5$ V until the activation curves were reproducible (φ-potential relative to a hydrogen electrode clamped to the same membrane). The nature of the curves is preserved at all values of $\Delta\varphi/\Delta t$.† The difference at points with the same potential for different values of $\Delta\varphi/\Delta t$ can be attributed either to differences in the state of the platinum surface [3, 4], or to differences in the degree of passivation resulting from the adsorption of organic substances from the membrane when the given potential is reached. Decrease in the value of $\Delta\varphi/\Delta t$ below 0.86 mV/sec produced no change in the shape or position of the curve. The curves obtained at $\Delta\varphi/\Delta t \leq 0.86$ mV/sec therefore be taken as the steady-state curves.

Comparison of the $I-\varphi$ curves given in Fig. 2 with the $I-\varphi$ curves for platinum electrodes completely [3, 5, 6] or partly [7] immersed in sulfuric acid shows that the curves in Fig. 2 differ significantly from the former but show some similarity to the latter. The comparatively high values of the current densities (the working surface was assumed to be the surface of the end face of the electrode, see below) and the absence of total passivation of the process at a potential of 1.5 V in fact suggest that our system is a system with distributed parameters.

The distribution of the parameters is related to the formation, on the electrode surface, of a thin film of electrolyte which is pressed from the membrane and through which hydrogen diffuses, and also to differences in the accessibility of separate sections of the film with respect to the polarizing current. The generation of current at the electrode clamped to the membrane takes place in different ways depending on the properties of the membrane. In the case of the rough MK-40 membrane with low degree of swelling, current formation takes place almost entirely at the surface of the end face of the electrode.

Because of the rough nature of the surfaces of the membrane and the electrode, diffusion of gaseous hydrogen takes place between the end face of the electrode and the membrane. As a result, the polarization curves differ

* The potential jump at the boundary between the membrane and the concentrated KCl solution in the syphon of the calomel electrode can be neglected in a first approximation.

† In the present paper we shall not deal with the differences between the curves for the anodic and cathodic directions of the change in potential for MK-40 and MK-100 membranes.

TABLE 1. Ratio of the Currents Generated at the Electrode with Diameter 2 mm to the Currents at the Electrode with Diameter 1 mm at the Same Potentials (MK-40 Membrane)

Form of treatment, $\Delta\varphi/\Delta t$	Potential, V		
	0.25	maximum	1.25
Etching in aqua regia; 34 mV/sec	3.2	5.3	5.15
Ditto	3.4	5	4.3
Electrodes clamped to fresh membrane after operation; 34 mV/sec	4	3.3	3
Ditto, 0.415 mV/sec	3.5	3.5	3
Treatment with sodium carbonate, etching in aqua regia; 34 mV/sec	5.8	6.4	5.8
Mean	4.3	4.6	4.4

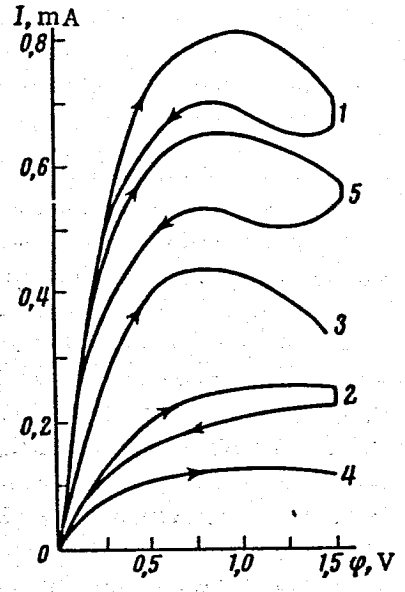


Fig. 3. Polarization curves obtained using electrodes with different diameters and MK-40 membrane: 1) d = 2 mm, $\Delta\varphi/\Delta t$ = 34 mV/sec; 2) d = 1 mm, $\Delta\varphi/\Delta t$ = 34 mV/sec; 3) d = 2 mm, $\Delta\varphi/\Delta t$ = 0.86 mV/sec; 4) d = 1 mm, $\Delta\varphi/\Delta t$ = 0.86 mV/sec; 5) d = 2 mm, $\Delta\varphi/\Delta t$ = 0.34 mV/sec; lateral surface sealed.

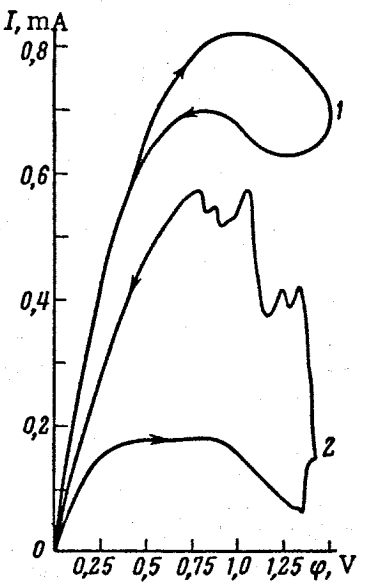


Fig. 4. Polarization curves obtained using MK-100 membranes and a platinum electrode with diameter 2 mm at $\Delta\varphi/\Delta t$: 1) 34; 2) 0.86 mV/sec.

little from one another (curves 1 and 5 in Fig. 3) for electrodes with an open lateral surface and with a lateral surface completely sealed into glass (the polished end face of the electrode in this case consisted of platinum and glass in the same plane). For the MK-40 membranes, the currents generated at electrodes with different diameters are proportional to the areas of their end faces (Table 1 and Fig. 3).

In this case we can assume the existence of thin films of electrolyte which are pressed from the membrane and lie on the surface of the microprojections of metallic platinum in contact with the microprojections of the MK-40 membrane.

If the space between the membrane and the end face of an electrode with completely sealed lateral surface is filled with twice-distilled water, i.e., if the supply of hydrogen to the platinum surface is restricted sharply, only the electrode surface is charged during polarization [1, 4]. Replacement of the atmosphere of hydrogen by an inert atmosphere (argon) in this case produces practically no change in the shape of the curves. This indicates that there is practically no diffusion of hydrogen through the membrane. The method can be developed to determine the permeability of the membranes with respect to hydrogen.

In the case of the MK-100 membranes, the overall appearance of the $I-\varphi$ curve (Fig. 4) is the same as that for the MK-40 membranes. The MK-100 membranes, however, have a higher degree of swelling, greater defor-

TABLE 2. Ratio of the Currents Generated at an Electrode with Diameter 2 mm to the Currents at an Electrode with Diameter 1 mm, Recorded at the Same Potentials, for MK-100 Membrane

Form of treatment; $\Delta\varphi/\Delta t$	Potential, V		
	0.25	maximum	1.25
Etching in aqua regia; 34 mV/sec	3.2	2.5	2.8
Ditto	2.05	1.65	1.8
Ditto	2.6	2.08	2.2
Ditto	2.2	1.79	2.5
Mean	2.28	2.0	2.35

mability, and smoother surface than the MK-40 membranes. As a result, the penetration of gaseous hydrogen between the end face of the electrode and the membrane is eliminated. Comparison of the currents at electrodes with different diameters and the same potentials shows that they are proportional to the perimeters (Table 2). In this case, generation of the current takes place under the film of electrolyte formed on the lateral surface of the electrode.

In the polarization of an electrode with completely sealed lateral surface, clamped to the MK-100 membrane, only the surface of the electrode is charged.

Thus the present work has not detected any fundamental difference between the processes of current formation at electrodes clamped to MK-40 and MK-100 membranes containing a certain quantity of sulfuric acid not absorbed by exchange, and familiar processes taking place at electrodes partially immersed in sulfuric acid. Further studies should reveal the specific features of this system, associated with the presence of the ion exchange membrane next to the electrode.

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LITERATURE CITED

1. O. A. Khazova, Yu. V. Vasil'ev, and V. S. Bagotskii, Élektrokhimiya, 1, 84 (1965).
2. W. G. French and Th. Kuwana, J. Phys. Chem., 68, 1279 (1964).
3. K. I. Rozental' and V. I. Veselovskii, Zh. Fiz. Khimii, 27, 1953 (1963).
4. F. G. Will and C. A. Knorr, Z. Elektrochem., 64, 258 (1960).
5. E. A. Aikazyan and A. N. Frumkin, Dokl. AN SSSR, 100, 315 (1955).
6. M. Breiter and M. Becker, Z. Elektrochem., 60, 37 (1956).
7. F. G. Will, J. Electrochem. Soc., 110, 148, 152 (1963).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of the first issue of this year.
