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

II. DEPENDENCE OF THE RATE OF THE PROCESS ON TEMPERATURE

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The electrochemical oxidation of hydrogen on platinum clamped to an ion exchange membrane is retarded by the presence of organic materials on the surface of the electrode. The hypothesis is put forward that the retardation is explained by the slowness of penetration of the reacting particles through the unusual type of adsorption layers on the surface.

The oxidation of hydrogen on a platinum electrode in the presence of a cation exchange membrane is one of the links in the current forming process in fuel cells with a membrane electrolyte. The dependence of the current removal in such cells on temperature was studied in a previous investigation [1], in which it was indicated that the electrode processes evidently determine the temperature changes in the operation of the cell as a whole. The method of investigation of the systems with ion exchange membranes developed by us [2], enables this problem to be explained more accurately and the temperature dependence of the individual electrode process to be characterized in the complicated system.

Investigations were carried out in a glass apparatus shown in Fig. 1. The apparatus was immersed in water, the temperature of which was maintained with an accuracy of ± 0.1°C.

The investigated electrode was a platinum wire of diameter 2 mm and length 5 mm which was clamped at the end to the membrane. The pressure of the electrode on the membrane was established by the help of a special device (see Fig. 1) and in all the experiments was about 20 kg/cm^2 on the surface of the electrode.

The reference electrode was a platinum–hydrogen electrode, clamped to the same membrane in the same way as the investigated electrode and the reference electrode was at a single temperature. During the investigations, cation exchange membranes of various types were used: IREA, MK-40, and OP6 (NIIPM). They were all preliminarily in the H^+ form and were leached for several months in bidistilled water periodically changed. The hydrogen, before introduction into the apparatus, was saturated with water vapors, the temperature of which was the temperature of the apparatus.

The change in temperature was from a higher to a lower temperature in the range from 45 to 15°C. With these changes, more reproducible results were obtained than with changes in temperature in the opposite direction. A decrease in temperature by 5° (which was the difference between the temperatures of two successive experiments) was carried out in 8 min, during which the polarization was switched off and the electrode had a potential of 0 V.

A comparatively small range in temperature, in which the investigations were carried out enables us to consider that the change in current with temperature in our experiments is indeed caused by the temperature coefficient of the rate of the electrode process and, to a first approximation, does not depend on the character of the temperature changes in the properties of the membrane.

The polarization curves were recorded in anodic and cathodic directions between 0 and 1.5 V with a rate of change of potential $\Delta\varphi/\Delta t$ = 52 mV/sec. The apparatus described in a previous investigation [2] was used for this.

The time between the anodic-cathodic cycles, i.e., the time for the electrode to remain at a potential of 0 V, was in the case of operation with membranes of IREA and MK-40 two minutes, and during operation with OP6 membrane five seconds. Repeating the cycles with the indicated intervals of time between them was carried out until the curves were superimposed one on the other (usually for this not more than six cycles were required). Such

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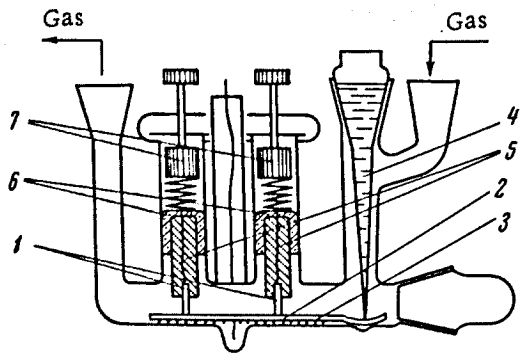


Fig. 1. Apparatus for measurements: 1) investigated electrode and reference electrode; 2) membrane; 3) auxiliary electrode (platinum grid); 4) siphon to external reference electrode; 5) polyethylene holders for the electrodes; 6) glass medical syringe; 7) device for changing pressure of the electrodes on the membrane.

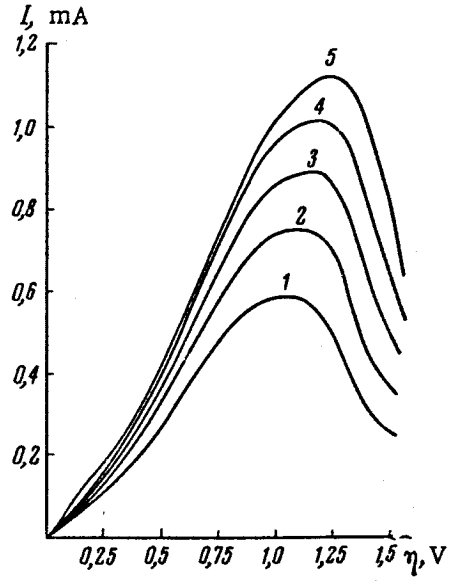


Fig. 2. Polarization curve for the ionization of hydrogen on a platinum electrode clamped to a IREA membrane, $\Delta\varphi/\Delta t$ = 52 mV/sec at temperatures of: 1) 20, 2) 25, 3) 30, 4) 35, 5) 40°C.

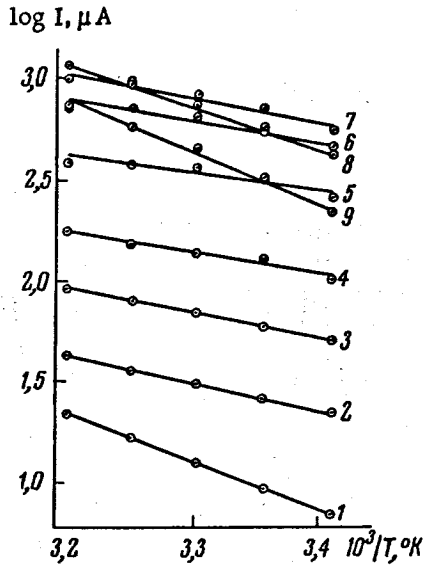


Fig. 3. Dependence of log I on 1/T, calculated from the polarization curves of Fig. 2 for the values of overpotentials of: 1) 0.03, 2) 0.06, 3) 0.125, 4) 0.25, 5) 0.5, 6) 0.75, 7) 1.0, 8) 1.25, 9) 1.5 V.

a treatment of the surface of the electrode by "cycling" results in a definite standard condition which differs from the initial condition which is established after a long period of time at 0 V.

Values for the apparent activation energy were calculated from polarization curves obtained during the first change in potential in the anodic direction after establishing a given temperature, i.e., after holding at 0 V for eight minutes, and also from polarization curves obtained during change of potential in an anodic direction after cycling.

Figure 2, as an example, gives anodic polarization curves of the reproducing cycles, obtained at various temperatures in experiments with IREA membrane and Fig. 3 gives the relationship between log I and 1/T, calculated from these polarization curves for definite values of overpotentials.

From the gradient of the straight lines of Fig. 3 and similar straight lines obtained from the results of other experiments not given here, the values for the apparent activated energy were calculated at various overpotentials.

The character of the relation between the apparent activation energy of the process of electrochemical oxidation of hydrogen on platinum and the overpotential was similar in experiments with membranes of different types. The $E-\eta$ curves have, as can be seen from Fig. 4, three characteristic portions. On the first portion (0-0.25 V), the initial value for the activation energy, which is the order of 10-15 kcal/mole, sharply decreases with increase in polarization. It may be thought that here the rate of reaction for oxidation of hydrogen is determined mainly by the so-called "activation" processes. On the second portion (0.25-0.9 V), the activation energy is practically independent of polarization—the rate of reaction is limited, not depending on the potential of the process of mass transfer (see below). The increase in activation energy with increase in polarization above 0.9 V (third portion), is obviously connected with the deposition of oxygen on the surface of platinum. It is of considerable interest that in the wide region of independence of the values of E on overpotential, i.e., approximately the region from 0.25 to 0.9 V, the value of E in all the experiments (except the experiments relating to curve 2 in Fig. 4c) is considerably greater than would be expected for pure diffusion limitations. This compels us to propose that, in the investigated systems, a phenomenon takes place similar to the effect of Loshkarev, who observed the change in kinetics of the electrode process and the appearance on the polarization curves of portions of independence of current on potential during the formation on the surface of the electrode of an adsorption layer of different thickness and composition, through which the reacting particles have to penetrate [3]. As is indicated in investigation [4], in the presence of the Loshkarev effect, a potential barrier arises caused by the necessity of the consumption of work for creation of "pores" in the layer for the introduction of the reacting particle. In this case, the stage of penetration may become the slowest and it is possible for the appearance of a limiting kinetic current for penetration practically independent of potential.

In the described system, the appearance of limiting currents was not observed as a result of the fact that the electrode operated as a partially immersed one (see [2]). Therefore, only the study of the temperature dependence enables the retardation connected with the penetration of particles through the adsorption layers be observed. The described phenomenon in our experiments was evidently caused by the nature of the organic compounds precipitated by the membrane electrolyte,

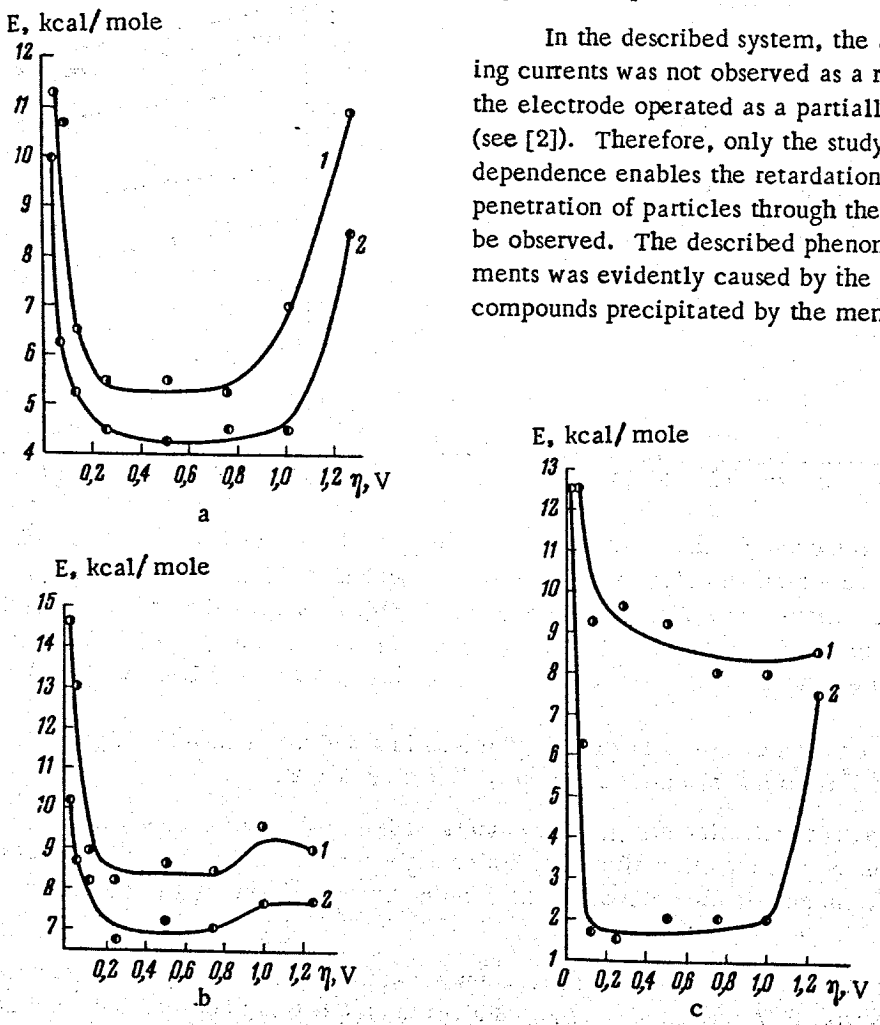


Fig. 4. Dependence of the apparent activation energy for ionization of hydrogen on platinum on the overpotential in the presence of the membranes: a) IREA, b) MK-40, c) OP6; curves (1) calculated from the anodic polarization curve before treating the surface by cycling; curves (2) the same after treating the surface with cycling.

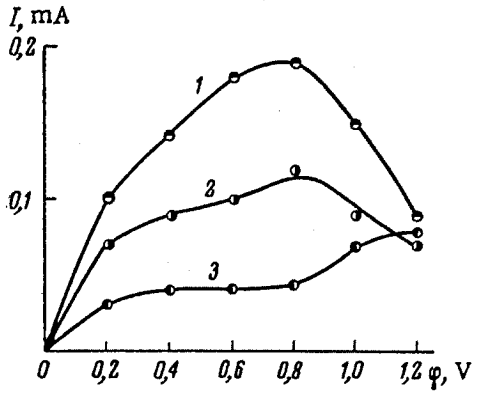


Fig. 5. Polarization curves for the ionization of hydrogen on a platinum electrode clamped to a IREA membrane. Preliminary polarization of the electrode before establishing the given potential was 15 sec. The potentials of preliminary polarization: 1) 1.5, 2) 0, 3) 0.7 V. Temperature 20°C.

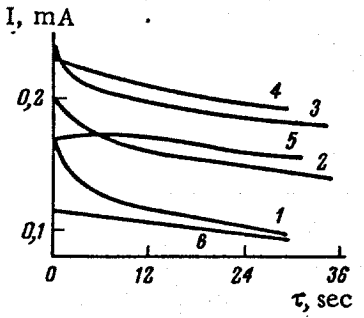


Fig. 6. Change in current of ionization with time at potentials of: 1) 0.2, 2) 0.4, 3) 0.6, 4) 0.8, 5) 1.0, 6) 1.2 V. Preliminary polarization of the electrode at 1.5 V before establishing the given potential was 15 sec. IREA membrane. Temperature 20°C.

which were capable of being adsorbed on the electrode surface. However, it is not excluded that it is caused by the presence at the surface of the electrode of the ion exchange electrolyte itself, i.e., the difficulty of the introduction of the ion of hydrogen into the volume of the membrane.

On comparing curves 1 with curves 2 on Fig. 4 it can be seen that the activation energy before carrying out the cycling is always greater than afterwards. On the middle parts of all curves of Fig. 4, where the activation energy does not depend on polarization, this difference is more marked and reaches approximately 8 cal/mole for the curves of Fig. 4c (in this case, the intervals of time between the cycles was the least). The difference in the values of the activation energies on curves 1 from the values on curves 2 may be connected with the different average thicknesses of the layers of organic material deposited on the surface of the electrode with $\eta = 0$ and, correspondingly, with the greater or less consumption of energy on the passage of the reacting particles through this layer. The confirmation of the retardation of the electrode process because of adsorption of organic material is given by the polarization curves on Fig. 5. Experiments on the ionization were carried out on the described platinum electrode, clamped to the IREA membrane. The electrode was polarized for 15 sec at potentials of 1.5, 0.7, and 0.0 V, after which the corresponding potential for the polarization curve was established. The change in the currents with time during this is given in Fig. 6 for one example; in this case, the electrode was preliminarily held at a potential of 1.5 V. The values of the current for the polarization curves in all cases were taken 30 sec after establishing the given potential, when their change had moderated.

Curve 3 of Fig. 5 obtained during the preliminary polarization of the electrode at 0.7 V (the potential at which the adsorption of organic materials is high [5]), lies below Curves 1 and 2.

It should be noted that the kinetics of oxidation of hydrogen on electrodes clamped to membranes of the various types are somewhat different (see Fig. 4a-c). This, naturally, is as a result of differences in the chemical composition both of the membranes themselves and of the products which are extracted from them and are adsorbed on the surface of the electrode. Identification of the composition and determination of the structure of these products is an extremely complex problem.

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