CHARGING CURVES OF A PLATINUM ELECTRODE IN SOLUTIONS OF PHOSPHORIC ACID AT VARIOUS TEMPERATURES

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A study of the electrochemical properties of platinum in solutions of phosphoric acid was begun comparatively recently, in connection with attempts to use phosphoric acid as an electrolyte in fuel cells. As was detected in [1, 2], at the potentials of the "double-layer" region, a maximum of the current is observed on the potentiostatic curve of a platinum electrode in phosphoric acid, the presence of which was explained by ionization of the strongly bound hydrogen [1] or by the occurrence of "spontaneous polymerization" of phosphoric acid [2]. However, later Tacker [3] demonstrated that the maximum in the "double-layer" region is due to the presence of oxidizable impurities, possibly of organic nature, in the phosphoric acid.

This work presents the results of a measurement of the charging curve and potentiostatic curve on platinum in 1, 3, and 15 N H_3PO_4 at various temperatures.

The measurement procedure was described in detail in [4, 5]. In measurements in the region of temperatures up to 95°C, the cell was immersed in a water thermostat with accuracy of the temperature regulation ±0.1°C; at temperatures > 100°C, an air thermostat was used (accuracy of temperature maintenance ±2°C). We used Pt/Pt electrodes (in the form of a plate or grid with visible surface 2, 20, or 100 cm^2) and electrodes of Adams platinum, produced by cathodic reduction of platinum dioxide [6]. Before the experiment, the test electrodes were subjected to anodic and cathodic polarization in dilute, phosphoric acid. We used concentrated phosphoric acid, analytical grade, as the initial preparation. All the potentials φ_r were measured with respect to the reversible hydrogen electrode in the same solution at the temperature of the experiment.*

Figure 1 presents the charging curves, measured on a Pt/Pt electrode in commercial preparations of phosphoric acid, not subjected to any supplementary purification (curves 1 and 2). At potentials of the "double-layer" region, the curves exhibit a lag, which is especially pronounced at increased temperatures (curve 2); a substantial hysteresis is also observed between the anodic and cathodic paths of the curves. The nature of the phenomena was established in the following experiment. A large Pt/Pt electrode (100 cm^2), the potential of which was maintained close to ~500 mV at 95°C for an hour, while the solution was mixed with a stream of argon, was immersed in the test solution. The charging curves of the test electrodes, after the treatment of the solution described (Fig. 1, curves 3 and 4), indicated virtual absence of a lag at −500 mV and good reversibility of the processes of adsorption and desorption of hydrogen at various temperatures. The data obtained are evidence, according to [3], that the oxidizable impurities in the test solution exert a substantial effect upon the shape of the charging curves [5].

The charging curves and potentiostatic curves of a Pt/Pt electrode in 15 N H_3PO_4, subjected to electrochemical purification, are close to the corresponding curves in 1N H_2SO_4 in the "double-layer" region and the region of the potentials of adsorption of hydrogen (Figs. 2, 3); however, the deposition of oxygen in solutions of phosphoric acid begins at somewhat more anodic potentials than in solutions of sulfuric acid, in agreement with the data of [8]. With increasing phosphoric acid concentration, the beginning of the deposition of oxygen is shifted toward more anodic potentials, while the amount of oxygen formed decreases. In concentrated phosphoric acid, a form of oxygen that is firmly bound to the surface and is reduced earlier than the bulk of the oxygen can also be observed. With increasing phosphoric acid concentration, the overvoltage of the liberation of gaseous oxygen increases.

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*As was indicated in [7], difficulties arise in realizing a reversible hydrogen electrode in concentrated phosphoric acid. Before the experiment, the reference electrode, as which we used a Pt/Pt grid, was subjected to anodic and cathodic polarization in the test solution at the temperature of the experiment. This operation proved sufficient for normal functioning of the hydrogen electrode.

M. V. Lomonosov Moscow State University. Translated from Élektrokhimiya, Vol. 3, No. 8, pp. 962-965, August 1967. Original article submitted November 24, 1966.

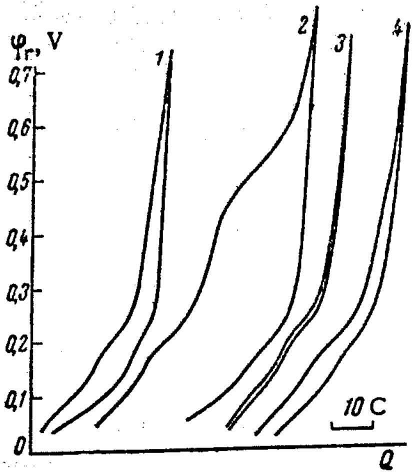

Fig. 1. Charging curves of a Pt/Pt electrode in 15 N H_3PO_4, analytical grade (1, 2) and purified electrochemically (3, 4) at 20°C (1, 3) and 95°C (2, 4).

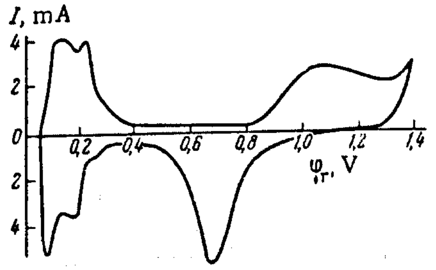

Fig. 2. Potentiostatic curve of a Pt/Pt electrode in 15 N H_3PO_4 at 20°C. Rate of development 16 V/h.

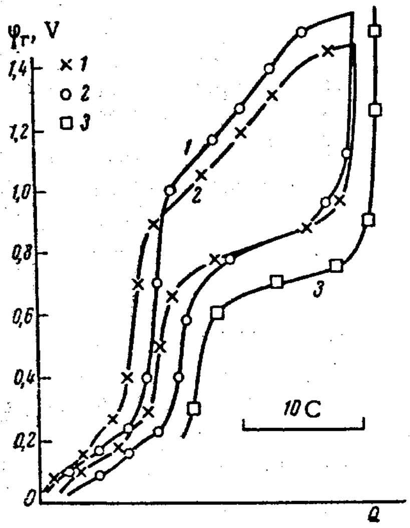

Fig. 3. Charging curves of Adams Pt at 20°C in 1N H_2SO_4 (1) and 15 N H_3PO_4 (2, 3). Curve 3 was measured after oxidation of the electrode at 180°C.

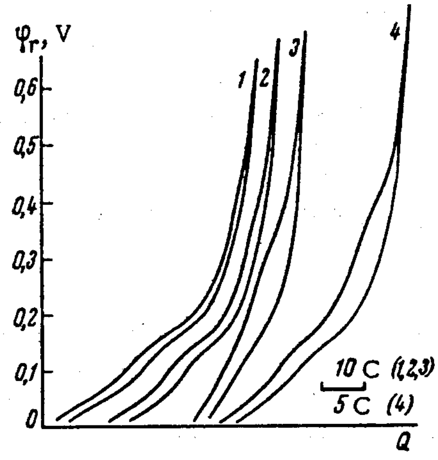

Fig. 4. Charging curves of Adams Pt in 15 N H_3PO_4 at 125° (1), 150° (2, 4), and 180°C (3). Curve 4 was measured after exposure of the electrode for 20 min at $\varphi_r = 0$.

Heating of a Pt/Pt electrode in 15 N H_3PO_4 to 200°C leads to a great reduction of the surface (approximately tenfold in comparison with a freshly platinized electrode). Moreover, a substantial deterioration of the reversibility of the charging curves is observed. We conducted an experiment with heating of a Pt/Pt elecrrode in the absence of the electrolyte in an atmosphere of argon. On the charging curves measured after this, the forward and reverse paths also differ greatly, which was also noted earlier [9].

The difficulties associated with sintering could be avoided by the use of an electrode of Adams platinum [5, 6]. As was shown by the experiments, heating of an electrode of Adams platinum at 200°C does not lead to any change in the properties of the electrode, although it is accompanied by a reduction of the surface. However, measurements at temperatures above 100°C on Adams Pt led to the conclusion of a need for further purification of solutions of phosphoric acid. When the temperature was increased, lags again began to appear on the charging curves in the double-layer region, the potential of which was shifted in the cathodic direction with increasing temperature, while the length increased. The degree of distortion proved to depend upon the degree of purity of the solution.

The best results at t° up to 150°C (Fig. 4) were obtained with solutions of phosphoric acid, used directly after the following treatment.* For several days, the acid was subjected to cathodic polarization on a mercury electrode (10 cm^2) with a current of 1 mA. Then the solution was purified for a long time by cathodic polarization on a Pt/Pt grid.† At higher temperatures, the distortions still remained (Fig. 4, curve 3), although they were substantially smaller than in the original solution.

The effectiveness of the cathodic polarization of solutions of H_3PO_4 on mercury evidently means that the impurities that cause a distortion of the shape of the charging curves are inorganic. These may be metallic cations, which in the presence of high cathodic potentials are reduced to the metal on a mercury electrode. The strong influence of many metallic cations upon the charging curves and properties of platinum is known from [10-12]. Our measurements also permit us to assume that the glass of the electrolytic cell can serve as a source of contamination of the solutions at high temperatures [7].‡ This is evidenced by the increase in the lag in "doublelayer" region after prolonged heating of the electrolyte at high temperatures in a measuring cell.

The total charging curves were measured in purified phosphoric acid on a Pt/Pt electrode and on Adams Pt (Fig. 3). With increasing temperature in H_3PO_4 solutions, as well as in H_2SO_4 solutions [4], simultaneously with the earlier oxidation of the surface, the strength of the bond of the adsorbed oxygen to the surface increases. This is evidenced by the close values of the potentials of the plateaus of reduction of oxygen at various temperatures, as well as by the fact that the reduction of surface oxides, formed at 180°C, occurs at 20°C with a large overvoltage (Fig. 3, curve 3).

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*Treatment of the H_3PO_4 solution with hydrogen peroxide [7] in our experiments was not effective.

†However, the purification described did not permit complete avoidance of contamination, since prolonged exposure of the electrode at 150°C in the region of the potentials of the adsorption of hydrogen still led to the appearance of distortions on the charging curves (Fig. 4, curve 4).

‡However, we were unable to observe any significant differences in the results of measurements in a cell of glass No. 23 and in a Pyrex glass cell.