# EFFECT OF POTENTIAL ON THE DISSOLUTION RATE OF PLATINUM IN HYDROCHLORIC ACID SOLUTIONS

(UDC 541.138.2)

A. N. Chemodanov, I. K. Morozova, V. V. Gorodetskii, M. A. Dembrovskii, V. V. Losev, and Ya. M. Kolotyrkin

L. Ya. Karpov Scientific Research Physicochemical Institute

Translated from Zashchita Metallov, Vol. 1, No. 4, pp. 433-435, July-August, 1965
Original article submitted February 28, 1965

It is well known [1-4] that platinum is dissolved with 100% yield with respect to the current in solutions of hydrochloric acid at potentials at which the oxidation of chlorine ions can be neglected ($\varphi$ < 1.1-1.2 V with respect to the normal hydrogen electrode). This dissolution proceeds by the reaction

$$Pt + 6Cl^- = PtCl_6^{2-} + 4\bar{e}. \quad (1)$$

Within this range of potentials the dissolution rate increases with increasing potential, increasing concentrations of chlorine ions, increasing acidity of the solution, and increasing temperature.

It is also well known [5] that at more positive potentials platinum is passivated in HCl solutions, but there are no published data on the dissolution of platinum under these conditions.

The purpose of our investigation was to determine the steady rate of anodic dissolution of smooth platinum in hydrochloric acid solutions within a wide range of potentials.

The measurements were made by the radiochemical method developed earlier [6]. Platinum samples (foil 0.05 mm thick) were activated by a neutron beam ($1.2 \cdot 10^{13}$ neutrons/cm$^2$ ·sec for 20-60 h) and were then subjected to anodic polarization. After this, the electrolyte was poured out and analyzed for the amount of radioactive platinum with a $\gamma$-spectrometer. The dissolution rate was calculated by comparing the sum of the number of pulses (subtracting the background pulses) for this solution in the 10 channels of the spectrometer within the interval of the 0.07 MeV energy peak (which corresponds to the platinum isotopes) and the corresponding sum of the number of pulses for a calibrated solution. The calibrated solution was prepared by dissolving platinum samples irradiated

Yields of Anodic Dissolution of Platinum with Respect to the Current (0.5 cm$^2$) in 10.2 N HCl

| Current, A·10$^6$ | Potential, V | Polarization time, min | Temperature, °C | Amount of platinum dissolved, g·10$^6$, determined by the radioactivity | Amount of platinum dissolved, g·10$^6$, determined by the current | No. of single layers of platinum removed (calculated by the current with respect to visible surface) | Yield with respect to the current, % |
|---|---|---|---|---|---|---|---|
| 14,1 | 0,93 | 32 | 25,5 | 13,7 | 13,6 | 64 | 100,5 |
| 14 | 0,925 | 28,5 | 25,5 | 12,6 | 12,1 | 57 | 104 |
| 14 | 0,935 | 32 | 25,5 | 13,7 | 13,6 | 64 | 101 |
| 14 | 0,93 | 28 | 25,5 | 12,6 | 11,9 | 56 | 106 |
| 800 | 0,955 | 15 | 80 | 355 | 364 | 1714 | 98 |
| 800 | 0,955 | 15 | 80 | 372 | 364 | 1714 | 102 |
| 800 | 0,955 | 15 | 80 | 386 | 364 | 1714 | 106 |
| | | | | | | Average | 102,5 |

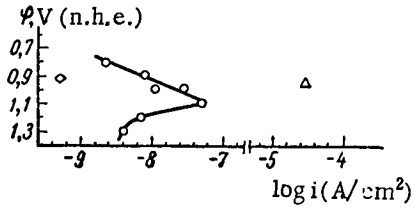


Fig. 1. Dependence of the steady dissolution rate of platinum in 1 N HCl on the potential. The dots and the triangle correspond to the dissolution rates in 0.1 and 10.2 N HCl solutions respectively.

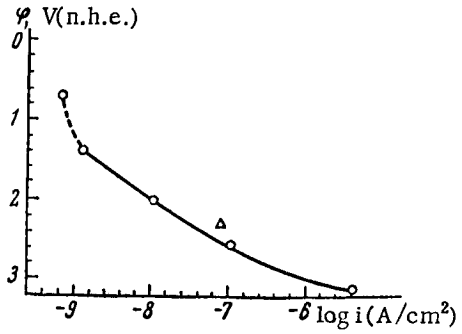


Fig. 2. Dependence of the steady dissolution rate of platinum in 0.1 N HCl + 3 N $HClO_4$ on the potential. The triangle indicates the rate of dissolution in 1 N HCl + 3 N $HClO_4$.

simultaneously with the anode completely in aqua regia; the solutions obtained were diluted to the desired concentration.

The experiments were made at room temperature. The electrode potential was calculated by the normal hydrogen scale without taking diffusion potentials into account. Before the experiments, the electrodes were etched in hot concentrated nitric acid, where a few tens to a few hundreds of single layers of the metal were removed. For each value of the potential the electrodes were polarized until the dissolution rate became constant. The time of the interruptions of the electrolysis to remove the samples from the solution analysis did not exceed 1-3 min.

To determine the possible effect of radioactive impurities present in the irradiated platinum and capable of passing into the solution and thus affecting the results of the analysis, we measured the dissolution rate of radioactive platinum under conditions where all the current was spent on the dissolution process ($\varphi \simeq 0.93$ V). * The yields of platinum dissolved in 10.2 N HCl at 25.5 and 80°C are shown in the table. The yields were calculated as the ratio between the amount of platinum which passed into the solution (determined radiochemically) and the amount of platinum calculated by the Faraday law, taking into account the valence of the ions formed [Eq. (1)]. The table showns that the results of radiochemical analysis coincide (within the limits of the experimental error) with the calculated results, and, consequently, the yield of platinum with respect to the current is 100%, in accordance with the published data. Thus, one obtains correct results by radiochemical determination of the rate of dissolution of platinum with the $\gamma$-spectrometer without preliminary removal of radioactive impurities from the solution, particularly gold.

Figure 1 shows the potentiostatic curve of dissolution of platinum in 1 N HCl at room temperature. As in the case of more concentrated solutions, the steady rate of the process is an exponential function of the potential in the region of active dissolution ($\varphi < 1.1$ V). Further displacement of the potential toward more positive values decelerates the reaction, which proceeds at a rate of $4 \cdot 10^{-9}$ A/cm² at a potential of 1.3 V. It was shown for the first time in [2] that this deceleration is due to the adsorption of oxygen on the platinum surface.

Let us note that within the region of active dissolution, the rate of the process is strongly dependent on the concentration of the acid. At the potential of 0.92 V, the steady rate of dissolution of platinum in 0.1 N HCl is negligibly small and does not exceed $5 \cdot 10^{-10}$ A/cm².

On the other hand, the table shows that in a 10.2 N HCl solution the rate of the process at the same potential reaches $3 \cdot 10^{-5}$ A/cm².

For comparison, Fig. 1 also shows the results obtained in a 1 N HCl solution.

Figure 2 shows the results of measurements of the steady dissolution rates of platinum in 0.1 N HCl at 1.4-3.1 V. Aside from the values obtained as the result of anodic polarization, we drew on this figure the point corresponding to the rate of spontaneous dissolution of platinum in the absence of external polarization ($\varphi = 0.7$ V). One can see that the rate of dissolution of platinum increases sharply with increasing potentials. Thus, when the potential is shifted from 1.4 to 3.1 V the rate of dissolution increases by a factor of 3000.

According to our preliminary results, the concentration of chlorine ions in this range of potentials has much less effect on the stability of the dissolution rate of platinum and in the region of active dissolution (see point for 1 N HCl in Fig. 2). Apparently, this effect indicates that the dissolution of platinum anodes within the passive

*T. N. Sokolova helped with the measurements.

region follows a different mechanism than in the active region, where the rate of dissolution is strongly dependent on the concentration of chlorine ions. We may assume that at high positive potentials the passage of platinum into solution is facilitated as the result of strengthening of the bonds of surface platinum atoms with oxygen and a deeper penetration of oxygen into the surface of platinum. Possibly, chloride complexes of platinum are formed in this case not directly during the electrochemical stage but as the result of a secondary chemical reaction.

Thus, the sharp increase of the rate of dissolution of platinum at potentials more positive than 1.4 V can be considered as a particular type of overpassivation due to the change in the mechanism of anodic dissolution in a way similar to that observed for other metals susceptible to passivation [7, 8].

## LITERATURE CITED


1. G. Grube, Z. Elektrochem., 35, 703 (1929).
2. B. V. Érshler, Zh. fiz. khimii, 14, 357 (1940).
3. A. Rius, J. Llopis, and I. M. Tordesillas, An. Real. Soc. esp. fis. y quim, 48B, 23, 193, 639 (1952).
4. T. Dickinson, R. C. Irwin, and W. F. K. Wynne-Jones, J. Electroanalyt. Chem., 7, 297 (1964).
5. M. Margules, Ann. phys., 65, 629 (1898); R. Ruerz, Z. phys. Chem., 44, 81 (1903).
6. V. V. Gorodetskii, M. A. Dembrovskii, and V. V. Losev, Zh. prikl. khimii, 36, 1543 (1963).
7. Ya. M. Kolotyrkin and V. M. Knyazheva, Zh. fiz. khimii, 30, 1990 (1956).
8. V. V. Losev and B. N. Kabanov, Zh. fiz. khimii, 28, 914 (1954).


---

**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 this issue.**

---