INFLUENCE OF THIOUREA ON THE CORROSION BEHAVIOR OF A PLATINIUM ANODE IN PERCHLORIC ACID

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Data are cited on the influence of additions of thiourea (TU), as well as sulfide and thiocyanate on processes of dissolution of metals and evolution of oxygen on a Pt anode in perchloric acid solutions at potentials 1.7-2.7 V (normal hydrogen electrode). An inhibiting effect of thiourea, due to sulfur-containing products of its destruction at the C–S bond was established. The possibility of local dissolution of a Pt anode is discussed.

In the presence of thiourea, the rate of dissolution of platinum in perchloric acid at high anodic potentials decreases [1]. In view of the necessity of increasing the corrosion resistance of platinum anodes, this phenomenon has been investigated in more detail.

The rate of dissolution of platinum was determined, combining electrochemical and radiochemical measurements with the use of γ-spectrometers. The method was described in [2, 3]. The electrodes were samples of platinum foil, and PlI (99.99% Pt), 20 μ thick. The perchloric acid was cp grade; thiourea was introduced into the solution directly before the experiment. The experiments were conducted in a clamped three-electrode cell without a diaphragm with a flow of electrolyte and a thermostatically controlled anode (50°). At each potential within the investigated region (1.7-2.8 V) the electrode was exposed in the supporting electrolyte (without additive) until the establishment of equilibrium conditions of dissolution. Then, without interrupting the polarization, the electrolyte with the additive was introduced into the cell. After the establishment of the rate of dissolution, the electrolyte with the additive was replaced by the supporting

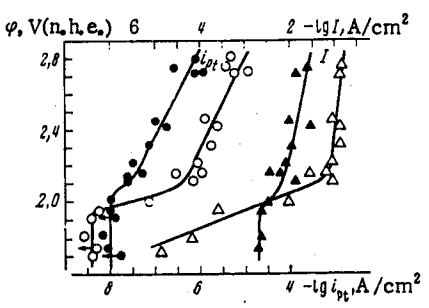

Fig. 1

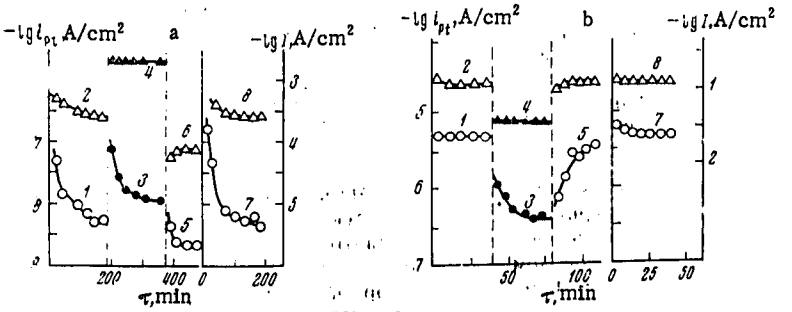

Fig. 2

Fig. 1. Partial curves of dissolution (○, ●) and static polarization curves (△, ▲) measured in 3 N $HClO_4$ (○, △) and 3 N $HClO_4$ + 1.5 $\cdot 10^{-2}$ M $(NH_2)_2CS$ (●, ▲).

Fig. 2. Variation with time of the rate of dissolution (1, 3, 5, 7) and anodic current density (2, 4, 6, 8) at φ = 1.9 V (a) and φ = 2.7 V (b) in 3 N $HClO_4$ (1, 2, 5, 6, 7, 8) and 3 N $HClO_4$ + 1.5 $\cdot 10^{-2}$ M $(NH_2)_2CS$ (3, 4); 7,8) after anodic–cathodic treatment of the electrode.

L. Ya. Karpov Physicochemical Scientific-Research Institute. Translated from Zashchita Metallov, Vol. 10, No. 6, pp. 684-687, November-December, 1974. Original article submitted January 30, 1974.

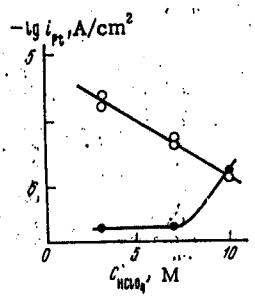

Fig. 3

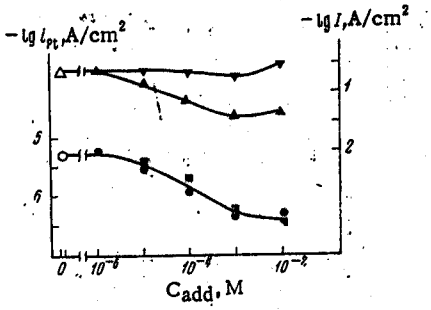

Fig. 4

Fig. 3. Influence of the $HClO_4$ concentration on the rate of dissolution at $\varphi = 2.7$ V in solutions without the additive (○) and with addition of $1.5 \cdot 10^{-2}$ M $(NH_2)_2CS$ (●).

Fig. 4. Influence of the concentration of $(NH_2)_2CS$ (●, ▲) and Na_2S (■, ▼) on the dissolution (●, ■) and current (▲, ▼) in 3 N $HClO_4$ at $\varphi = 2.7$ V.

electrolyte without changing the conditions of polarization, and the rate of dissolution was again measured. Then the electrode was subjected to electrochemical treatment according to the standard procedure (3 N $HClO_4$; anodic polarization, 3-10 min at $\varphi = 3.0$-3.1 V; cathodic polarization, 30 sec at $\varphi = -0.05$ V), after which the rate of its dissolution in the supporting electrolyte at the same potential was again determined. The potentials were measured relative to the normal hydrogen electrode. Polarization was carried out from P-5827 and P-5848 potentiostats. Figure 1 shows that the inhibiting effect of thiourea is manifested only in the region of $\varphi > 1.95$ V. At lower polarizations, this introduction even leads to a certain increase in the rate of dissolution* and the polarizing current density. At high anodic potentials, when oxygen is intensively liberated, the decrease in the current under the influence of thiourea is due to an inhibition of this process. The reverse effect at lower potentials is related to the occurrence of a reaction of oxidation of thiourea.† A change in the sign of the effect occurs at the same potential ($\varphi = 1.95$ V) as for the process of dissolution.

As an illustration, Fig. 2a, b cites typical curves of the dependence of the rate of dissolution of platinum and the polarizing current density on the time of exposure of the electrode at potentials below and above 1.95 V. As can be seen, after polarization in a solution with the additive, the anodic current and rate of dissolution in the supporting electrolyte (curves 5 and 6) are found to be lower than the corresponding static values, measured before the introduction of thiourea into the electrolyte (Fig. 2, curves 1 and 2). The "aftereffect" of thiourea noted is of a kinetic nature and is maintained for a shorter time, the higher the electrode potential. After standard electrochemical treatment, the electrode entirely regains its original corrosion and electrochemical properties (compare curves 1, 2 and 7, 8).

Evidently, in the case of anodic polarization in a solution with additive, the surface of the electrode is covered by products of oxidation of thiourea, which effectively inhibit both the process of anodic dissolution of platinum and the reaction of liberation of oxygen. The presence of a distinct parallelism in the changes of dissolution of platinum and the rate of evolution of oxygen agrees with the earlier conclusion of an interrelatedness of these processes [3, 4].‡ The removal of inhibiting particles from the surface of the anode in the background electrolyte is facilitated when the potential is displaced in the positive direction. Noteworthy is the fact that for the process of dissolution after polarization in the solution with thiourea, the degree of inhibition in the supporting electrolyte, as a rule, is higher than for the liberation of oxygen, while the time necessary for reaching equilibrium conditions of dissolution is greater (Fig. 2, b, curves 5 and 6).

*Here and henceforth the rate of dissolution is expressed in units of apparent current density. It is assumed that platinum passes into solution in the tetravalent state.

†In the potential region $\varphi = 1.7$-1.9 V, the process of oxidation of thiourea proceeds with a diffusion control.

‡In the region $\varphi \leq 1.9$ V, the dissolution of platinum in an electrolyte with an addition of thiourea evidently proceeds according to a different mechanism, not associated with the liberation of oxygen.

It can be assumed that under the conditions considered, the processes of dissolution of the metal and evolution of oxygen proceed nonuniformly (there are regions on the surface of the electrode with an increased corrosion and electrochemical activity); moreover, the first process is localized to a greater degree than the second.* The same regions (or sites) on the surface are evidently also most active with respect to the process of adsorption of inhibitors, since they are blocked primarily by the oxidation products of thiourea, and are freed from them with the greatest difficulty in the case of anodic polarization of the electrode in the supporting electrolyte.

With increasing perchloric acid concentration, the rates of dissolution and evolution of oxygen at high anodic potentials decrease, and there is a simultaneous decrease of the inhibiting action of thiourea. As can be seen from Fig. 3, the rate of dissolution of platinum in 10 N $HClO_4$ at $\varphi = 2.7$ V is practically independent of the presence of thiourea. It can be assumed that an increase in the volume concentration of perchloric acid promotes a decrease in the surface concentration of oxidation products of thiourea.

For a judgment of what products of the oxidation of thiourea inhibit the processes of dissolution of platinum and evolution of oxygen, we conducted some experiments with solutions containing additions of sulfide and thiocyanate. Within a broad range of concentrations, hydrogen sulfide has approximately the same inhibiting influence on the process of dissolution in 3 N $HClO_4$ at $\varphi = 2.7$ V, as thiourea (Fig. 4). On the other hand, in 10 N $HClO_4$, when $\varphi = 2.8$ V sulfide ($4.2 \cdot 10^{-3}$ M) and thiocyanate ($2 \cdot 10^{-3}$ M) practically do not change the rate of dissolution. Thus, regardless of the nature of the investigated sulfur-containing additives, their effect on the process of dissolution at high anodic potentials is entirely analogous. Evidently the oxidation of thiourea, like that of the thiocyanate anion, proceeds at least partially with cleavage of the C–S bonds, so that particles of sulfur or its conversion products are responsible for the inhibition of the process of dissolution in perchloric acid.

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*A quantitative estimation of the degree of localization of the process of dissolution, which may be associated with the inhomogeneity of the platinum surface and with the presence of nonmetallic inclusions, does not seem possible at the present time.