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ADSORPTION AND ELECTROOXIDATION OF SULFUR DIOXIDE ON PLATINUM*)

By

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Abstract

The sulfur dioxide adsorption and anodic oxidation processes on platinized platinum in the pH range 0.3~12.9 have been studied by the radioisotope method and voltammetry. It has been found that at all pH, SO_2 electrooxidation proceeds to sulfuric acid without intermediate formation of dithionic acid. The reaction mechanism depends significantly on the kind of pretreatment of platinum surface.

One of the vital tasks of energetics is conversion of the heat energy produced in nuclear reactors into other kinds of energy. In combined thermoelectrochemical cycles the nuclear reactor heat is used for hydrogen production. A promising thermoelectrochemical cycle is the so-called sulfuric acid cycle (the Westing-house cycle).[1] This cycle includes thermolysis of sulfuric acid followed by electrochemical water decomposition, depolarizing the anodic process with sulfur dioxide. Platinum is an active catalyst of the electrochemical oxidation reaction of sulfur dioxide.[2]

The mechanism of the sulfur dioxide anodic oxidation reaction on platinum has been more than once discussed in literature.[3~7] In diluted acid solutions at low polarization values there seems to occur direct electron transfer from adsorbed SO_2 molecules to the electrode, followed by interaction of cation radicals with water[3]:

$$SO_{2\,ads} - e \longrightarrow SO_{2\,ads}^{+} \qquad (1)$$

$$SO_{2\,ads}^{+} + 2H_2O - e \longrightarrow HSO_4^{-} + 3H^{+} \qquad (2)$$

At large anodic polarization values when platinum surface is covered with oxides there occurs mainly chemical oxidation of SO_2 by the oxide oxygen.[3,4] The influence of pH on the mechanism of this reaction has not been studied.

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It was suggested recently[8,9] that SO_2 oxidation proceeds via intermediate formation of dithionic acid:

$$2SO_2+2H_2O-2e\longrightarrow H_2S_2O_6+2H^+ \qquad (3)$$

This suggestion is beased on the bimolecular reaction order with respect to SO_2 oxidation on platinized platinum in concentrated sulfuric acid (44 wt %). In the above-mentioned works no data are given on the adsorption of sulfur dioxide and its hydration products on the platinum electrode surface. Recently in[10] the SO_2 adsorption on Pt in 0.5 M H_2SO_4 was investigated by the radioisotope method.

In the present paper I want to acquaint you with the studies carried out at the Institute of Electrochemistry by the author and M. R. Tarasevich, K. A. Radyushkina, O. A. Levina, V. N. Andreev. They investigated by the radioisotope method and voltammetry the SO_2 adsorption and anodic oxidation processes on platinized platinum in the pH range 0.3~12.9. On the basis of the obtained adsorption and kinetic dependences a scheme is proposed of the sulfur dioxide anodic oxidation process on a Pt electrode.

The adsorption and electrocatalytic properties of the Pt electrode surface with respect to molecules and ions containing S(IV) depend significantly on the state of its surface. Treatment (activation) of a Pt electrode in the potential range $E\div 0.05\sim 1.2$ V in solution with or without SO_2 leads tc radically different adsorption and kinetic dependences.

1. Sulfur dioxide adsorption

Kinetic studies of the SO_2 adsorption on a Pt electrode (not activated in the presence of SO_2) in the potential range $E\div 0.4\sim 0.6$ V*) showed that the time necessary for the steady state SO_2 adsorption to be reached is ~10 min. The chemisorption of sulfur-containing particles is strong: at $E=0.5$ V no desorption of appreciable amounts of sulfur-containing particles in 0.5 M H_2SO_4 was observed during 30 min. The behavior in the adsorbed layer of the SO_2 adsorption product accumulated on Pt at $E=0.5$ V when the potential changed in the range $E\div 0.0\sim 1.5$ V is shown on Fig. 1 for pH= 0.3 (Curves 1, 2) and 12.9 (Curve 3). It can be seen from Fig. 1 that in acid and alkaline solutions the adsorbed particle is not removed from Pt surface when E shifts from 0.5 to 0.0 V, but is desorbed from the surface at $E>0.5$ V due to oxidation. When the solution pH increases from 0.3 to 2 the amount of adsorbed sulfur-containing particles decreases by one half. In the pH range 2~12.9 the amount of adsorbed particles remains practically

*) Here and below the potentials are referred to the standard hydrogen electrode.

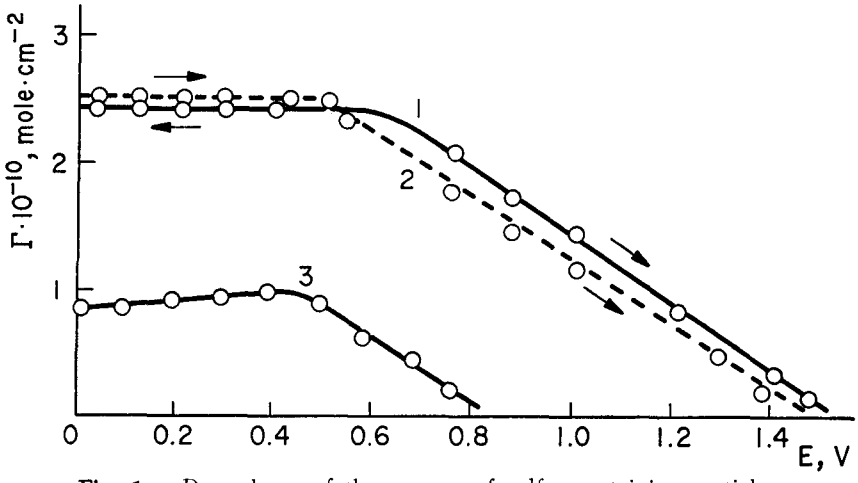

Fig. 1. Dependence of the amount of sulfur-containing particles adsorbed on Pt at 0.5 V from solutions 10^{-2} M Na_2SO_3+ 0.5 M H_2SO_4 (Curves 1, 2) and 10^{-2} M Na_2SO_3+0.5 M NaOH (Curve 3) and remaining in adsorbed state when the electrode potential shifts in 0.5 M H_2SO_4 (1, 2) and 0.5 M NaOH (3) from 0.5 to 0.0 V and further to 1.5 V (1) or from 0.5 V to 1.5 V (2, 3).

the same. These phenomena seem to be due to a higher adsorptivity of neutral SO_2 and H_2SO_3 molecules as compared to the anions HSO_3^- and SO_3^{--}.

The dependence of the amount of adsorbed sulfur-containing product on the Pt electrode potential measured directly in adsorbate solution after steady state adsorption in reached at $E=0.5$ V is shown on Fig. 2. It is clear that with increasing anodic potential ($E \geqslant 0.8$ V) adsorption decreases. The electrode potential shift in the cathodic direction (Fig. 2, Curve 1) is accompanied by increases in the amount of sulfur-containing product on the electrode. The subsequent shift of E from 0.0 V to 1.5 V leads to decrease of adsorption, but the amount of adsorbed particles remaining on the electrode is much larger than that observed in the case of Curve 2, Fig. 2. The sulfur-containing adsorption product accumulated on Pt at $E \sim 0.0$ V is strongly bound with the surface. When the adsorbate solution is replaced by 0.5 M H_2SO_4 and the Pt electrode is kept in it for 30 min. at E in the range from 0.0 to 0.5 V adsorbed particles do not undergo desorption. Oxidation of adsorbed substance under galvanostatic conditions showed that $\sim 5.7\ e^-$ is expended in oxidation of one sulfur-containing particle of the product*).

*) $2.6\ e^-$ are consumed in oxidation of the product accumulated on the Pt electrode at $E=0.5$ V and $\sim 3.5\ e^-$ per a sulfur-containing particle in its reduction at $E=0.0$ V.

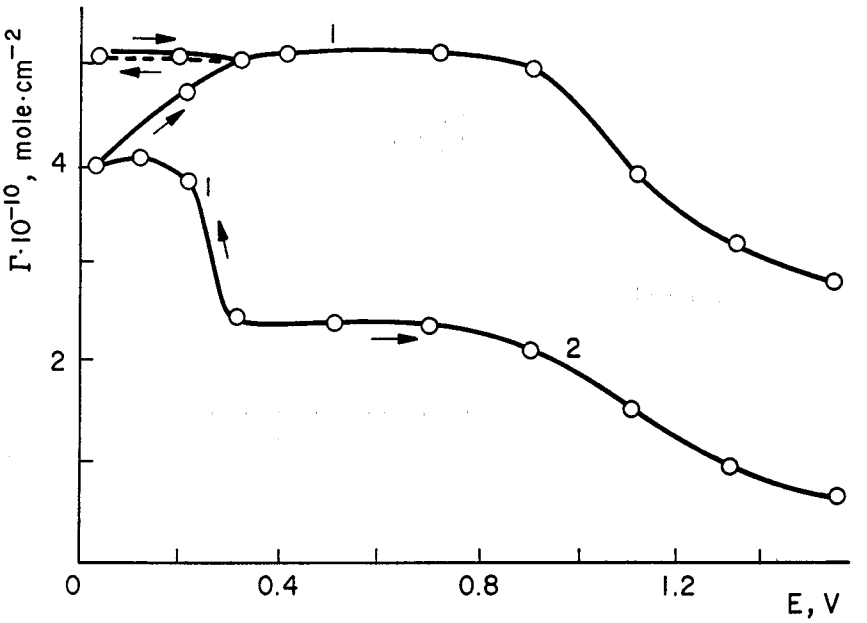

Fig. 2. Dependences of the steady state adsorption values of sulfur-containing particles on Pt electrode potential measured in 10^{-2} M Na_2SO_3+0.5 M H_2SO_4 solution. Potential of the beginning of adsorption −0.5 V. Curve 1 measured when E shifted from 0.5 V to 0.0 V and further to 1.5 V. Curve 2 measured when E shifted from 0.5 V to 1.5 V.

The product can be completely removed from the Pt electrode surface only by prolonged anodic-cathodic polarization (~60 min) with the current 0.25 mA·cm^{-2} in the potential range 0.0~1.5 V in solution without SO_2.

The surface coverage of the Pt electrode with sulfur-containing product, determined from the hydrogen region of the charging curve was 0.36 at E_{ads}=0.5 V and 0.50 at E_{ads}=0.05 V. The amounts of sulfur-containing products present on the electrode were 2.5×10^{-10} and 5.1×10^{-10} mole·g^{-1}, respectively. Thus when the extents of adsorption of sulfur-containing particles differed by 100%, the surface coverages differed only by 30%. This fact can indicate that during adsorption SO_2 interacts with the Pt electrode surface not only directly but also through the already adsorbed product, *e. g.* by formation of $S-S$ bridges.

In alkaline solutions the Γ, E dependences for a Pt electrode activated in solution with or without SO_2 similar (see Fig. 1, Curve 3). This seems to be due to the fact that the anion SO_3^{--} is not reduced.

2. Sulfur dioxide electrooxidation

Fig. 3 shows the polarization curves of SO_2 oxidation at different pH on a Pt electrode previously activated in solution without SO_2. The curves were measured from the steady-state potential established on the electrode at given pH up to $E=1.2$ V. It can be seen that at all pH the curves show a plateau where current practically does not depend on potential. The values of the current on this plateau depend on the rate of rotation of the electrode, but they are much lower than the theoretical limiting diffusion currents for a two-electron reaction. Apparently, in this potential range oxidation of particles containing S(IV) proceeds by way of their interaction with Pt surface oxides. The rate of their formation and the activity depend

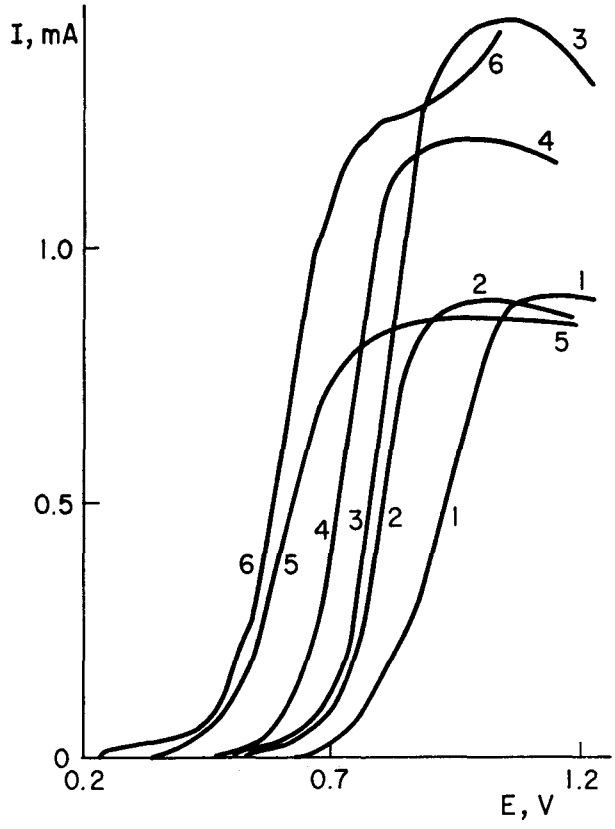

Fig. 3. *I*, *E* dependences for the SO_2 electrooxidation reaction on Pt previously activated in solution without SO_2: pH, 1–0.3, 2–2.6, 3–3.1, 4–4.9, 5–7.6, 6–12.

on the ionic composition of solution. This seems to explain the different height of the limiting kinetic current in solutions of different pH. At pH= 0.3~3 the value of $\partial E/\partial \lg i$ is 100 mV and at pH>3 it rises to 120~150 mV (Table).

TABLE Kinetic parameters of the SO_2 anodic oxidation reaction on a Pt electrode

Electrode	pH	$\partial E/\partial \lg i$	$\partial E/\partial$ pH	$\partial \lg i/\partial \lg C_{SO_2}$
1. Pt, activated in solution without SO_2	0.3–3	100	−50	
	3–7	120	−50	1
	7–12.9	150	0	
2. Pt, activated in solution with SO_2	0.3–3	60	−30	
	3–7	120	+30	1
	7–12.9	150	0	

Increase of pH from 0.3 to 7 leads to increase of the sulfur dioxide electrooxidation reaction rate. Here the value $\partial E/\partial$ pH is 50 mV. When pH rises from 7 to 12.9 the reaction rate remains unchanged (Fig. 4, Curve 1, Table). In the SO_2 concentration range from 10^{-4} to 10^{-2} mole/ℓ the reaction is of the first order with respect to SO_2 concentration.

The polarization curves of SO_2 oxidation at different pH on a Pt electrode previously activated in the potential range 0.05~1.2 V in solution with SO_2 are shown on Fig. 5. It is clear from comparison of Figs. 3 and 5

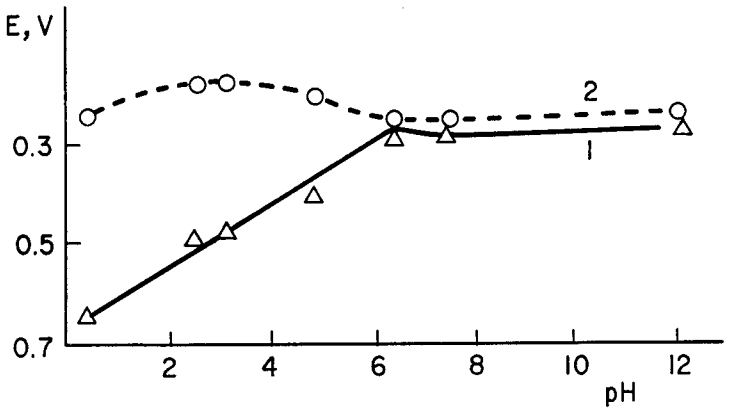

Fig. 4. Dependence of potential at $I=200\ \mu$A on pH for Pt electrode activated at $E=0.05$–1.2 V in solution without SO_2(1) and with SO_2(2).

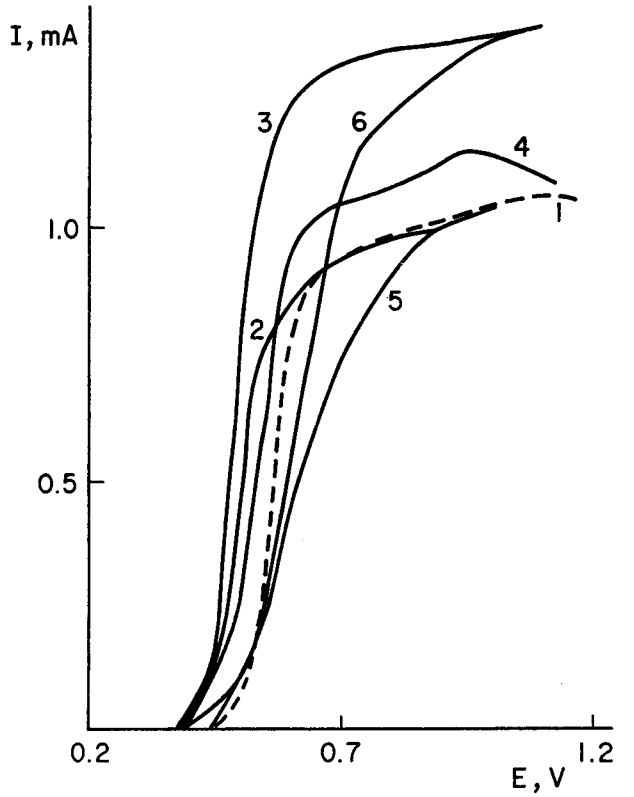

Fig. 5. *I*, *E* dependences for the SO_2 oxidation reaction on Pt previously activated in solution with SO_2, pH: 1–0.3, 2–2.6, 3–3.1, 4–4.9, 5–7.6, 6–12.

that in the case of Pt electrodes activated in solution with SO_2, the rate of anodic oxidation of SO_2 increases considerably. In solution with pH from 0.3 to 6 after activation in the presence of SO_2 the *I*, *E* curves shift in the cathodic direction by 300 mV. For more alkaline solutions (pH $\div$ 6 $\sim$ 12.9) the influence of activation on the reaction rate is insignificant. The kinetic parameters $\partial E/\partial \lg i$ and $\partial E/\partial$ pH also change (Table). In the pH range from 0.3 to 3 the value of $\partial E/\partial \lg i$ is 60 mV and at pH $>$ 3 it rises to 120 $\sim$ 150 mV. After activation of the Pt electrode in the presence of SO_2 the dependence of the SO_2 electrooxidation rate on pH also changes: $\partial E/\partial$ pH is equal to $\pm$30 mV in the pH range 0.3 $\sim$ 7 (*i. e.* it is practically independent of pH) and does not depend on pH at pH $>$ 7 (Fig. 4, Curve 2, Table).

A complex combination of the kinetic parameters (Table) and their

variation with the experimental conditions seem to be due to a difference in the structure of reacting particles and different types of their coordination on the Pt electrode surface. The data obtained by the radioisotope measurements show that the state of the Pt electrode surface activated in the presence or absence of SO_2 in solution is different. In the latter case, under the conditions of SO_2 oxidation, the Pt surface is covered by sulfur.

It is known[11] that in aqueous sulfur dioxide solutions the type of particles varies with pH: at $pH<2$ mainly neutral SO_2 and H_2SO_3 molecules are contained in solution; at $2<pH<5$ there are present the anions HSO_3^- and at $pH>6$ — the anions SO_2^{2-}.

The experimental data obtained in the present study, namely the first reaction order with respect to the SO_2 concentration and absence of dithionic acid in solution, indicate that on Pt in diluted solutions SO_2 electrooxidation proceeds to sulfuric acid without intermediate formation of dithionic acid. The mechanism of this reaction depends essentially on the kind of platinum surface pretreatment.

On platinum not activated in the presence of SO_2 all particles undergo oxidation: SO_2, H_2SO_3, HSO_3^-. The reaction rate increases when passing from neutral (SO_2, H_2SO_3) to negatively charged (HSO_3^-, SO_3^{--}) particles. Since in the pH range from 0.3 to 7 the reaction is of fractional order with respect to the hydrogen ion concentration ($\partial \lg i/\partial \lg C_{H^+}=0.5$) it can be assumed that the adsorption of the particle being oxidized is accompanied by its deprotonation on the electrode surface:

$$H_2SO_3 \rightleftharpoons HSO_{3\,ads}^- + H^+$$

$$(HSO_3^- \rightleftharpoons SO_{3\,ads}^{--} + H^+)$$

The slow step includes the first electron transfer from the coordinated particle to form a radical or a cation radical:

$$HSO_{3\,ads}^- \rightarrow HSO_3^{\cdot} + e$$

$$(SO_{3\,ads}^{--} \rightarrow SO_3^{-\cdot} + e)$$

This reaction course leads to experimentally observed dependences $\partial E/\partial \lg i = 100 \sim 120$ mV and $\partial E/\partial pH = -50$ mV. In solutions with $pH>7$ only deprotonated particles are present, which leads to independence of the reaction rate of pH.

In contrast, on Pt surface covered by sulfur at $pH<3$ a different type of coordination is observed, leading to dehydration of adsorbed particles. The adsorbed particles are bound with platinum surface through a sulfur atom. This creates favorable conditions for charge transfer along the *S-S*

bridge, which leads to general acceleration of the reaction. The first electron transfer step seems to be a reversible one. Under the conditions such as these the rate-determining step is either a subsequent chemical reaction of interaction of the radical or the cation-radical with the oxygen-containing particles, or the second electron transfer.

At pH>3 the mechanism of sulfur dioxide electrooxidation on platinum activated or not activated in the presence of so_2 seems to be the same.

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