MECHANISM OF ELECTROCHEMICAL OXIDATION

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I. INTRODUCTION. THEORETICAL IDEAS ON THE MECHANISM OF PROCESSES AT HIGH ANODE POTENTIALS

A characteristic of electrochemical processes at high oxidation potentials is the clearly expressed role of chemical interaction between the electrode and oxygen atoms and radicals formed during the electrolysis and having a high chemical activity. This chemical interaction of active particles with the electrode not only complicates processes at high electrode potentials, but is a necessary condition of their occurrence and determines the mechanism of the processes. Chemical specificity in electrochemical oxidation appears in the interaction of surface oxygen (anionic) compounds with the discharging ion in the elementary electrochemical act. The electrical field at the electrode – solution boundary acts (lowering the activation energy) on both the discharging ion and the surface oxygen (anionic) compound.

In electrochemical oxidation processes proceeding with a change in the oxygen balance of the ions (molecules), as a rule oxygen passes from the surface oxygen compounds, where it may be in a chemically active state (chemosorbed oxygen atoms and hydroxyl radicals) and under the influence of the electrical field of the double layer. The character of the surface compounds is determined both by the chemical nature of the system and by the electrode potential and substantially affects the selectivity of a given electrode reaction in the whole electrochemical process. The selectivity of an electrochemical process (the ratio of the rates of possible reactions in the whole electrochemical process) is determined by the probability of the interaction of a given discharging ion with a given component of the surface compound at the given electrode potential. Attempts to develop theoretical ideas on the mechanism of electrochemical oxidation (evolution of oxygen) starting from the premise that the rate-determining stage is the recombination of oxygen atoms (decomposition of oxides) and also elementary ideas on the determining role of ion discharge cannot explain experimental material and do not lead to satisfactory solutions [1, 2].

Experimental investigations of the state of actual electrode surfaces carried out over the last 25 years, to a large extent by Soviet electrochemists, make it possible to put forward the ideas formulated above on the determining role of surface electrode compounds in the mechanism and kinetics of electrochemical processes and, in particular, electrochemical oxidation processes [2]. Assuming that the stage determining the rate of electrochemical oxidation processes (beginning with the simplest process, namely the liberation of oxygen) is the interaction of chemosorbed oxygen (anion or hydroxyl radical) and the discharged ion under the action of the electric field with the formation of the corresponding molecule or oxidize ion, it is possible to explain the experimental rules very fully, especially for stationary processes of electrochemical oxidation (liberation of oxygen) at high current densities:

$$\mathrm{Me \cdot MeO\,[O]_{ads} + A^- - \mathit{e} \xrightarrow{\varphi} Me \cdot MeO + AO.}$$

$$\mathrm{Me \cdot MeO\,[OH]_{ads} + A^- - \mathit{e} \xrightarrow{\varphi} Me \cdot MeO + AOH.}$$

where A^- is an anion and the other symbols have their usual meaning.

The state of the oxidized electrode is represented in the most typical form: MeO denotes the stable oxides of the electrode metal; $[O]_{ads}$ is chemosorbed oxygen and $[OH]_{ads}$ is an adsorbed hydroxyl radical, participating in the electrode process. In addition to the role of the surface oxygen (anionic) compounds in the selectivity of the process emphasized above, the scheme presented reflects the mechanism of the production of an oxygen overvoltage, which is localized not only in the ionic double layer but also in the layer of dipoles of adsorbed oxygen atoms, hydroxyl radicals or discharging anions (of the $[SO_4]$ type, see p. 248). On the basis of these concepts, the initial equation for the kinetics of the electrochemical liberation of oxygen in alkali will have the form

$$i = k_1 [\mathrm{OH}^-]\, e^{\frac{\alpha F}{RT}(\varphi-\varphi_1)} \cdot [\mathrm{OH}]\, e^{\frac{\beta F}{RT}\varphi_1}.$$

The surface concentration of hydroxyl radicals is a function of the electrode potential: $[OH] = f(\varphi)$; however, at high current densities there are sufficient grounds for taking the surface concentration of radicals as constant and then, after simple rearrangement, we obtained for the overvoltage

$$\eta = k + \frac{\alpha-1}{\alpha}\frac{RT}{F}\ln[\mathrm{OH}^-] + \frac{\alpha-\beta}{\alpha}\varphi_1 + \frac{RT}{\alpha F}\ln i,$$

or for a given solution at constant temperature after combination of the constants

$$\eta = a + b\ln i + c\varphi_1.$$

The three-term equation obtained for the oxygen overvoltage describes the experimentally established rules much more accurately. The new constant $c = \frac{\alpha-\beta}{\alpha}$ makes a quantitative allowance for the difference in the efficiency of action of the electric field on the discharging ion (characterized by the constant α) and on the adsorbed radical – dipole (characterized by the constant β). The jump in potential φ_1, included in the total value of the overvoltage with the coefficient c, equals the value of that portion of the overvoltage of the "electrode" part of the overvoltage which results from the ionic double layer. The above allowance for the complex structure of the double layer in the production of an oxygen overvoltage and the appearance of the value φ_1 due to the dipoles of electrochemically active surface electrode compounds bears a formal analogy to the allowance for the value of the ζ-potential (or ψ_1-potential) in electrode kinetics, which arises as a result of the diffuseness of the ionic part of the double layer. Where the surface oxygen compounds of the electrode are semiconducting, due to the low concentration of electrons in these compounds the distribution of potential through the depth of the electrode will also obey an exponential law [3].

II. NEW EXPERIMENTAL DATA SUBSTANTIATING THE IDEAS PUT FORWARD

Experiments with labeled oxygen (O^{18}) were carried out to obtain a direct answer to the problem of the participation of surface oxygen compounds of the electrode in the electrochemical liberation of oxygen on a Pt-electrode from an aqueous solution of H_2SO_4 [4]. Surface oxygen compounds enriched in O^{18} were first formed on a Pt-electrode by electrolysis in an aqueous solution of H_2SO_4 enriched with heavy oxygen; then the first portions of oxygen, liberated electrochemically from a normal (not enriched in O^{18}) solution, were assayed mass-spectrometrically for O^{18}. The results of the experiments are presented in the table.

From these data it follows that the oxygen isotope O^{18} introduced into the surface oxides of the Pt-electrode, formed at a potential of $\varphi \approx 1.45$ — 1.5 v, is detected in the first portions of oxygen in subsequent electrolysis of a normal (unenriched) aqueous solution of H_2SO_4. Exchange of the oxygen of the oxides with the electrolyte can only lead to a decrease in the effect observed. The data obtained indicate that the higher surface oxygen compounds of platinum participate in the electrochemical liberation of oxygen. It also follows from the table that the surface oxygen compounds of platinum formed at a potential of $\varphi \approx 0.9$ v do not participate in the electrochemical liberation of oxygen. Thus, on the basis of the experimental data obtained we can assume the existence of the following stage in the electrochemical liberation of oxygen on a Pt-electrode, which essentially affects the over-all rate of the process and the value of the overvoltage on the electrode:

Results of Experiments With Labeled Oxygen*

O^{18} content of water, %	Potential of Pt-electrode after the end of polarization in solution enriched O^{18} v	O^{18} content of gaseous oxygen in normal solution, %			O^{18} content of standard sample of oxygen, %
		first sample	second (next) sample	third sample	
1,2	0,9	0,200	—	—	0,201
1,2	0,9	0,197	—	—	0,197
1,2	1,2	0,198	—	—	0,197
1,8	1,2	0,198	—	—	0,195
1,2	1,5	0,245	0,240	0,216	0,197
1,2	1,46	0,235	0,225	0,185	0,185
1,2	1,47	0,240	0,215	0,198	0,199
1,8	1,5	0,362	0,278	0,236	0,201
1,8	1,5	0,340	0,285	0,245	0,201
1,8	1,45	0,286	0,250	0,213	0,201

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* All potentials in the present work are relative to the potential of a normal hydrogen electrode.

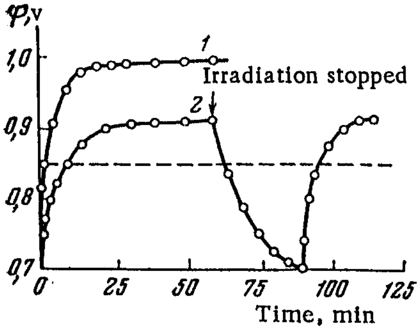

Fig. 1. Change in potential of Au electrode in 0.8 N H_2SO_4 under the action of γ-radiation: 1) in an oxygen atmosphere; 2) in a nitrogen atmosphere. Mechanism: $Au \cdot AuO + OH \rightarrow Au\ AuO[OH]$; $Au \cdot AuO[OH] \rightarrow AuAuO^+ + OH^-$.

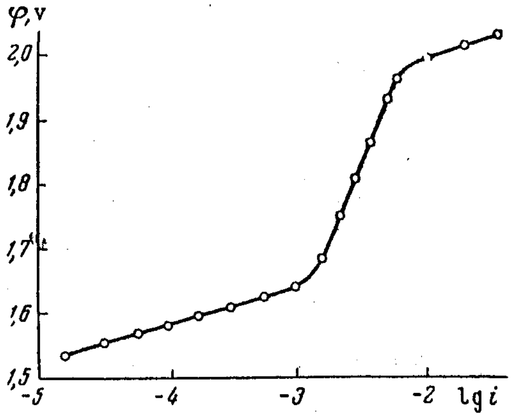

Fig. 2. Curve of oxygen overvoltage on an Ag electrode in 1 N NaOH.

$$Pt \cdot PtO[O] + H_2O - 2e \xrightarrow{\varphi} Pt \cdot PtO + O_2 + 2H^+$$

or

$$Pt \cdot PtO[OH] + H_2O - e \xrightarrow{\varphi} Pt \cdot PtO + {}^1/_2 O_2 + H^+ + H_2O.$$

The recombination scheme likewise does not contradict the experimental data presented; however, on the basis of all available material it can be considered less probable, especially for high current densities.

The nature of the surface oxygen compounds formed on an electrode during electrolysis is of very great interest. In addition to classical electrochemical methods of investigating the properties of these compounds [5], photogalvanic methods have been used for determining the electrical and electrochemical parameters of surface oxygen compounds [6]. We present data on a behavior of an Au-electrode in H_2SO_4 solutions under the action of γ-radiation, indicating adsorption of OH radicals, equivalent to oxidation of the electrode [7].

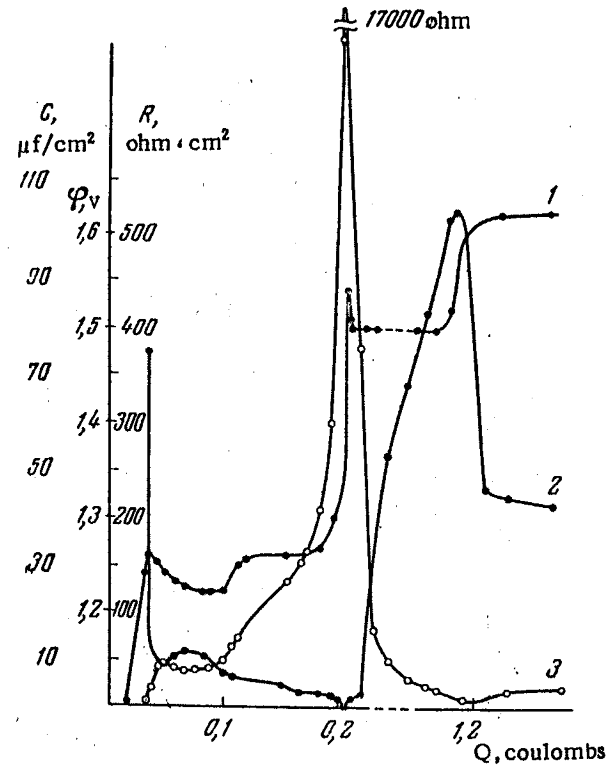

Fig. 3. Anode charging curve of an Ag electrode in 1 N NaOH (1) and the change in differential capacity (2) and resistance (3) of an Ag electrode with the amount of electricity passed. The curves were obtained by measuring in alternating current; frequency 200 cps.

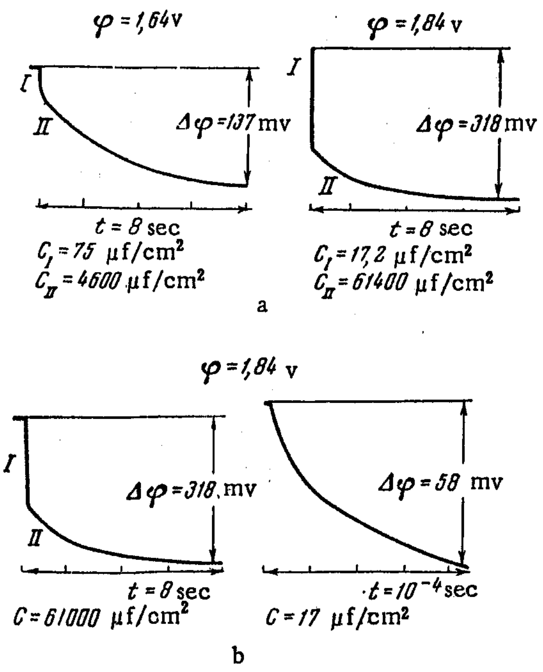

Fig. 4. a and b. Curves of the fall in potential on an Ag electrode in 1 N NaOH after switching off the polarizing current.

As is known, in the case of the action of γ-radiation OH radicals appear in solution as a result of the of the radiolysis reaction

$$H_2O \xrightarrow{h\nu} H + OH;$$

they may be adsorbed by the electrode and lead to the corresponding potential determining process:

$$Me + OH \rightarrow Me\,[OH]_{ads}$$
$$Me\,[OH]_{ads} \rightleftarrows Me^+ + OH^-.$$

Adsorbed hydroxyl radicals evidently may be liberated during electrolysis as a result of the primary discharge act. Fig. 1 gives data on the change in potential of a gold electrode in an aqueous solution of H_2SO_4 under the action of γ-radiation in oxygen and nitrogen atmospheres and also the value of the potential produced in this system by 0.01 N hydrogen peroxide for comparison (broken line). Analysis of the results indicates that the components responsible for the sharp change in potential of the Au-electrode are hydroxyl radicals appearing in solution as a result of radiolysis, in accordance with the mechanism presented in Fig. 1. To accept adsorbed hydroxyl radicals as the electrochemically active component first formed on the electrodes is also tempting due to the possibility in this case of a simple explanation of the so-called consolidation (ageing) of electrochemically formed oxides according to the scheme

$$Me\,[OH]_n \rightarrow Me\,[O]_{n/2} + {}^1/_2\,n\,H_2O.$$

III. MECHANISM OF OXYGEN LIBERATION ON A SILVER ELECTRODE IN ALKALI

From the point of view of the ideas developed it seemed interesting to examine the electrochemical liberation of oxygen on a metal on which oxygen compounds have first been formed on the surface and in the bulk.

A. I. Krasil'shchikov investigated the mechanism of oxygen overvoltage on a nickel electrode [8]. New data obtained in our laboratory on the mechanism of the electrochemical liberation of oxygen on a nickel electrode were published recently [9]. Here we present new data on the mechanism of the electrochemical liberation of oxygen on an Ag electrode, obtained in our laboratory by A. A. Yakovleva and T. I. Borisova by different methods. Fig. 2 shows the relation between the potential of an anodically polarized Ag electrode in 1 N NaOH and the logarithm of the polarizing current density. The curve in Fig. 2 is characterized by two regions: at 1.55 – 1.7 v the slope of the curve is characterized by the value b ≃ 70 mv and at 1.90 – 2.1 v, by the value ~ 160 mv; at potentials above 2.0 v, the process is complicated by solution of silver oxides. It is necessary to take into consideration the fact that oxygen is liberated on an already oxidized silver surface. The parameters of oxides formed on an Ag-electrode during anode polarization are presented in Fig. 3. As is known [10], the charging curve (1) characterizes the amount of silver oxides formed on the electrode: these are of the Ag_2O type at a potential of ~ 1.2 v and of the $Ag_2O_2(AgO)$ type at ~ 1.45 v. Curves 2 and 2 were obtained during the plotting of the charging curve.

Fig. 4, a shows oscillograms of the fall in potential of an anodically polarized Ag-electrode in alkali at starting potentials of 1.64 and 1.84 v, referring to the first (sloping) and second (transitional) regions of the kinetic curve in Fig. 2. From the oscillogram of the fall we found the capacity of the $Ag \cdot Ag_2O \cdot Ag_2O_2$ electrode at the corresponding potential values, referring to the initial (I) and subsequent (II) falls. To calculate the capacity on section I we used data on the fall in potential in the first moment after switching off the current (see Fig. 4, b which gives the curve obtained after 10^{-4} sec). For an electrode with a starting potential $\varphi = 1.64$ v, the capacities were as follows: $C_1 = 75\ \mu f/cm^2$ (initial fall) and $C_2 = 4600\ \mu f/cm^2$ (subsequent fall); for an electrode with a starting potential $\varphi = 1.84$ v: $C_1 = 17\ \mu f/cm^2$ and $C_2 = 61\,400\ \mu f/cm^2$.

On the basis of the material presented the following mechanism is adopted for the electrochemical liberation of oxygen on an Ag electrode in alkali.

The first stage, common to all the potential regions of oxygen liberation

$$Ag \cdot Ag_2O \cdot Ag_2O_2 + OH^- - e \xrightarrow{\varphi} Ag \cdot Ag_2O \cdot Ag_2O_2[OH]$$

proceeds quite rapidly and does not limit the over-all rate of the process.

The second stage differs essentially in different potential regions: at $\varphi = 1.55 \rightarrow 1.7$ v b = 70 mv and the reaction proceeds according to the scheme

$$Ag \cdot Ag_2O \cdot Ag_2O_2[OH]_n \xrightarrow{\varphi} Ag \cdot Ag_2O \cdot Ag_2O_2 + \frac{n}{4} O_2 + \frac{n}{2} H_2O,$$

i.e., the stage determining the over-all rate of the process corresponds to the recombination mechanism. In the potential region $\varphi = 1.90 - 2.1$ v the following reaction is the most probable rate determining process:

$$Ag \cdot Ag_2O \cdot Ag_2O_2[OH]_n + nOH^- - ne \xrightarrow{\varphi}$$
$$\xrightarrow{\varphi} Ag \cdot Ag_2O + Ag_2O_2 + \frac{n}{2} O_2 + n\,H_2O,$$

i.e., the reaction corresponding to the so-called electrochemical mechanism of overvoltage.

The general form of the relation between the value of the oxygen overvoltage on a silver electrode in alkali and the polarizing current density may be expressed by equation (1) presented above.

IV. KINETICS AND MECHANISM OF THE ELECTROCHEMICAL OXIDATION OF CONCENTRATED H_2SO_4 SOLUTION WITH THE FORMATION OF O_2, $H_2S_2O_3$ AND O_3.

The present process not only gives material for assessing the participation of surface oxygen and anionic compounds in the production of an oxygen overvoltage on an electrode but also makes it possible to elucidate the role of these compounds in the selectivity of the process. A detailed account of the experimental material referring to the present section obtained in our laboratory was given in the report of A. A. Rokov, Ė. V. Kasatkin and K. I. Nosova in the present collection [11]. Here we will present only the basic ideas on the mechanism of the combined electrochemical formation of oxygen, persulfuric acid and ozone. Fig. 5 gives a characteristic polarization curve of a Pt-electrode in 10 N H_2SO_4 at t = -70°. It consists essentially of the following. The kinetics curve described has three characteristic regions: $\varphi \simeq 1.6 - 2.4$ v; $\varphi \simeq 2.8 - 3.4$ v and $\varphi \simeq 6.0$ v, which are quite clearly separated by regions of a sharp rise in potential. Analysis of the electrolysis products formed showed that the first region corresponded to the evolution of oxygen (> 96%), the second to the predominant formation of persulfuric acid (> 60%) and the third (high potential region) was marked by a high efficiency of ozone formation (up to 30%). Moreover, available literature data [12, 13] and also material from our laboratory on the state of the surface of a Pt-electrode in the system investigated showed that these polarization regions, characterized by a substantial difference in the composition of the electrolysis products, correspond to different states of the electrode surface. In the potential region 1.6 — 2.4 v, the surface of a platinum electrode is covered with higher surface oxygen compounds and the processes occurring here may be represented by the scheme:

$$\mathrm{Pt\cdot PtO} + \mathrm{H_2O} - e \xrightarrow{\varphi} \mathrm{Pt\cdot PtO[OH]_{ads}} + \mathrm{H^+}$$

$$\mathrm{Pt\cdot PtO[OH]_{ads}} + \mathrm{H_2O} - e \xrightarrow{\varphi} \mathrm{Pt\cdot PtO} + \frac{1}{2}\mathrm{O_2} + \mathrm{H_2O} + \mathrm{H^+}$$

or

$$\mathrm{Pt\cdot PtO} + \mathrm{H_2O} - 2e \xrightarrow{\varphi} \mathrm{Pt\cdot PtO[O]_{ads}} + 2\mathrm{H^+}$$

$$\mathrm{Pt\cdot PtO[O]_{ads}} + \mathrm{H_2O} - 2e \xrightarrow{\varphi} \mathrm{Pt\cdot PtO} + \mathrm{O_2} + 2\mathrm{H^+}$$

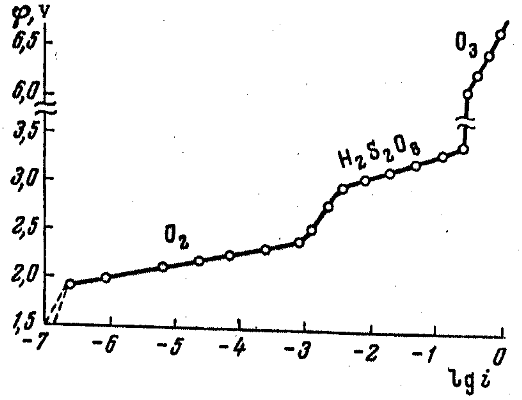

Fig. 5. Polarization curve of a Pt electrode in 10 N H_2SO_4 at -70°.

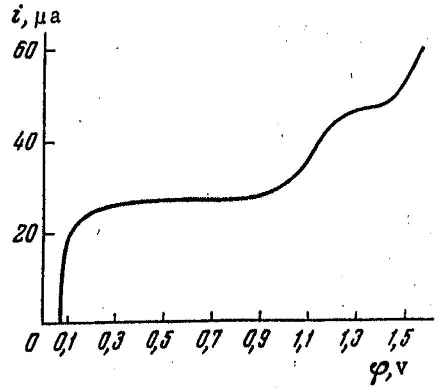

Fig. 6. Polarization curve of Pt electrode in a solution of uranium salts on 0.1 N $HClO_4$.

The problem of the nature of the surface adsorbed oxygen, involved in the production of the oxygen overvoltage, cannot be solved unequivocally by considering the available experimental material. On the basis of the ideas put forward in the first part of the present report and the combined experimental data it is assumed that in this case (Pt electrode in H_2SO_4) the stage determining the over-all rate of the process is the electrochemical desorption of oxygen, i.e., the formation of an O_2 molecule as a result of the discharge of the oxygen of a water molecule on adsorbed atomic oxygen (hydroxyl radical). The electrochemical generation of adsorbed atomic oxygen (hydroxyl radicals) in this region of potentials will apparently proceed rapidly and not limit the over-all rate of process.

The region of $\varphi \simeq 2.8$ -- 3.4 v on the kinetic curve, corresponding to the predominant formation of persulfuric acid, must be described by the following equations for the electrode reactions:

$$\mathrm{Pt\cdot PtO} + \mathrm{SO_4^{2-}} - 2e \xrightarrow{\varphi} \mathrm{Pt\cdot PtO[SO_4]_{ads}}$$

$$\mathrm{Pt\cdot PtO[SO_4]_{ads}} + \mathrm{SO_4^{2-}} \xrightarrow{\varphi} \mathrm{Pt\cdot PtO} + \mathrm{S_2O_8^{2-}}.$$

The transition region from a potential $\varphi = 2.4$ to $\varphi = 2.8$ v corresponds to electrochemical adsorption of SO_4 radicals (discharge of SO_4^{2-}) with the formation of an anionic surface compound; the stationary process of the electrochemical formation of persulfuric acid proceeds due to the interaction of SO_4^{2-} with surface adsorbed radicals of SO_4. The electrical field acts on both the sulfate ion and the chemosorbed radical.

In the region of high anode potentials where the electrochemical formation of ozone occupies a substantial position in the over-all process, the following reaction may be proposed

$$\mathrm{Pt\cdot PtO[O_2]_{ads}} + \mathrm{H_2O} - 2e \xrightarrow{\varphi} \mathrm{Pt\cdot PtO} + \mathrm{O_3} + 2\mathrm{H^+}.$$

In the electrode reaction schemes presented we have attempted to draw attention to the second side of the electrode process: the formation of surface oxygen and anodic compounds and their participation in electrochemical anode oxidation. Thus, on the one hand, consideration of the change in probability of discharge of various solution components with a change in the electrode potential, and on the other, consideration of the nature of surface electrode compounds formed, with which the discharging complex may react, make possible a deeper understanding of the complex processes of electrochemical oxidation.

It seemed interesting to determine how the over-all electrochemical oxidation process (the selectivity of the process) was affected by a change in the nature of the surface compounds, produced by introducing substances binding (or displacing) different surface-adsorbed components.

V. ELECTROCHEMICAL OXIDATION OF URANIUM IONS

The results of an investigation of the electrochemical oxidation of uranium on a platinum electrode [14] were particularly interesting in the light of the ideas on the mechanism of anode oxidation process examined. As is known, the most stable forms of uranium ion in aqueous solution under normal conditions are the hexavalent uranium (uranyl) ion, UO_2^{2+}, and tetravalent uranium, which has the structure U^{4+} or UO^{2+} in an acid solution. However, the electrochemical parameters in mixtures of hexa- and tetravalent uranium are also determined by the presence of pentavalent uranium, which is in equilibrium with hexa- and tetravalent uranium. The pentavalent uranium ion, UO_2^+, apparently differs from the hexavalent ion in charge alone (it differs from the tetravalent ion in amount of structurally bound oxygen also).

Fig. 6 shows a polarogram of the electrochemical oxidation of a mixture of tetra- and pentavalent uranium ions in aqueous perchloric acid solution. The first rise in the curve (at about $\varphi = 0.1$ v) corresponds to oxidation of pentavalent uranium and is close to the equilibrium potential of penta- and hexavalent uranium. Here the whole of the experimental data corresponds to the simplest process mechanism involving as electron transfer:

$$\mathrm{UO_2^+} - e \rightleftarrows \mathrm{UO_2^{2+}}.$$

The oxidation of the tetravalent uranium ion, which gives a polarographic wave with a half-wave potential $\varphi = 1.1$ v (see Fig. 6), is more complex. The half-wave potential thus differs from the equilibrium potential of a solution of tetra- and hexavalent uranium by about 0.7 v. The slope of the polarographic wave cannot be interpreted on the basis of electron discharge ideas either. Meanwhile, from independent investigations of the state of a Pt-electrode surface it is known that in this region of potentials the Pt-electrode is covered with adsorbed oxygen and an electrochemically active surface oxygen compound begins to form, which participates in the liberation of molecular oxygen, as was discussed above.

On the basis of these data, the following mechanism was adopted for the electrochemical oxidation of tetravalent uranium ions on a Pt-electrode:

$$\mathrm{Pt} + \mathrm{H_2O} - 2e \xrightarrow{\varphi} \mathrm{Pt[O]} + 2\mathrm{H^+};$$
$$\mathrm{Pt[O]} + \mathrm{UO^{2+}} \xrightarrow{\varphi} \mathrm{Pt} + \mathrm{UO_2^{2+}}$$

or

$$\mathrm{PtO} + \mathrm{H_2O} - 2e \xrightarrow{\varphi} \mathrm{PtO[O]} + 2\mathrm{H^+};$$
$$\mathrm{PtO[O]} + \mathrm{UO^{2+}} \xrightarrow{\varphi} \mathrm{PtO} + \mathrm{UO_2^{2+}}.$$

The nature of the chemically adsorbed oxygen cannot be defined more accurately from the data obtained. It is possible that the oxidation process involves hydroxyl radicals of the type Pt[OH] or PtO[OH] chemosorbed on the platinum and this would lead to a certain change in the oxidation mechanism but would not change established ideas on the active participation of surface oxygen compounds in the electrochemical oxidation of tetravalent uranium ions.

The elucidation of the detailed mechanism of electrode reactions is necessary for rational direction of the course of electrochemical reactions. An important task in electrochemistry at the present time is the establishment of the reasons determining the selectivity of an electrochemical process, i.e., the efficiency of a given electrode reaction in a complex electrochemical process. An examination of experimental material obtained by different methods for these types of electrochemical oxidation reactions leads to the conclusion that together with the magnitude and nature of the distribution of the electrical field, an essential factor determining the mechanism, rate and selectivity of an electrochemical oxidation process is the surface anionic (oxygen) compounds, whose nature depends on the substance and potential of the electrode and also the solution composition. Finding ways of effectively influencing the nature and properties of the surface electrode compounds is an important route to rational direction of an electrochemical process for obtaining the optimal yield of given electrolysis products in a complex electrochemical process.

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