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Abstract

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Application of the Tracer-Atom Method to the Study of the Mechanism of Anodic Oxygen Evolution

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On the basis of the results of a study of the mechanism of the process of oxygen evolution on a platinum electrode in concentrated solutions of sulfuric and perchloric acids at large anodic polarizations, the assumption was put forward that the acid anion participates in this process ([1]). We supposed that, in order to test such a view, the use of an acid labeled with the heavy isotope of oxygen, O^{18}, might prove effective.

It could be expected that the oxygen evolved during electrolysis of the labeled acid at small values of the overvoltage (up to 0.9 V) would not contain the heavy oxygen isotope, whereas the oxygen evolved at higher values of the overvoltage, following the sharp rise of the polarization curve (Fig. 1), caused by adsorption of the acid anion, would be enriched in O^{18}.

In the present communication we report the results of work in which O^{18}-labeled perchloric acid was used as the electrolyte. In doing so we were guided by the fact that, as follows from literature data ([2]), perchloric acid does not exhibit isotopic exchange of oxygen with water, whereas in the case of sulfuric acid such exchange takes place, especially at high temperature ([3]).

The labeled perchloric acid was prepared as follows: potassium perchlorate $KClO_4$ was prepared by anodic oxidation of potassium chloride in heavy-oxygen water (1.34% O^{18}) to potassium chlorate $KClO_3$, followed by oxidation of the latter, also in labeled water; the washed and recrystallized labeled potassium perchlorate was distilled with concentrated sulfuric acid (98%) under vacuum; in a cooled receiver, vapors of anhydrous perchloric acid condensed, which was purified by double distillation and diluted with ordinary twice-distilled water to the required concentration.*

Electrolysis of perchloric acid was carried out in an electrolytic cell in the form of a U-shaped tube with anodic and cathodic spaces separated by means of a glass filter. Into the anodic space were introduced a bridge for monitoring the anode potential during electrolysis and an outlet for the evolving oxygen. The oxygen was collected in a bell under water, after which it was transferred into an evacuated ampoule; beforehand the oxy—

* According to mass-spectrometric analysis, the content of the heavy oxygen isotope in the potassium perchlorate obtained was 1.34%, while in 5.8 N perchloric acid it was only 0.75%, and in 7.6 and 10 N perchloric acid, 0.836%.

To determine the reason for the decrease in the O^{18} content in perchloric acid compared with the labeled perchlorate used, sulfuric acid distilled from the mixture with perchloric acid remaining after preparation of the anhydrous perchloric acid was subjected to electrolysis. The oxygen evolved in this process proved to be enriched in the heavy isotope O^{18} by 0.074%. Thus the presence of isotopic exchange of oxygen between ClO_4^- and SO_4^{2-} anions upon heating dry potassium perchlorate with 97-98% sulfuric acid was established.

oxygen passed through a trap with a cooling mixture, in which the moisture was frozen out. In all cases, before collecting a sample, electrolysis was first carried out for 2 hr at the specified potential in order to fill the small air space in the anodic arm of the electrolyzer with the oxygen being evolved. The experiments were conducted at a temperature of $+20^{\circ}$, and in $10\,N$ chloric acid also at a temperature of -30°.

The results of isotopic analysis of the oxygen evolved during electrolysis of solutions of four concentrations at different values of the overvoltage are given in Table 1.

Examination of the data presented in Table 1 shows that the oxygen evolved at overvoltages up to 0.8 V contains no excess amount of O^{18}. This confirms the assumption stated earlier that at low anodic polarizations oxygen evolution occurs without participation of the acid anion, through decomposition of surface oxides and discharge of water. At higher overvoltages, corresponding to the upper portion of the polarization curve, the oxygen proves to be enriched in the heavy isotope O^{18}. At the same time, the O^{18} content increases with increasing concentration of the acid anion and with increasing overvoltage.

If the fraction of participation of the acid anion in the process of anodic oxygen formation is expressed by the ratio of the excess content of O^{18} in the oxygen evolved during electrolysis to that in the initial acid, then for small values of the overvoltage it is equal to zero, while for high overvoltages, for example 1.55-1.6 V, it is equal to 3.3% for $5.8\,N$ chloric acid, 18.5% for $7.6\,N$, and 78% for $10\,N$. This is clearly illustrated by Fig. 1, where values are given for the fraction of participation of the acid anion, in percent, as a function of the magnitude of the overvoltage at which electrolysis was carried out.

Thus, from the data obtained it follows that at high overvoltage values, corresponding to the upper portion of the polarization curve, a change occurs in the mechanism of oxygen evolution, caused by the participation of acid anions adsorbed on the electrode.

Fig. 1. Anodic polarization curves of a platinum electrode in chloric acid: 1—5.8 N, 2—7.6 N, 3—10 N

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Beck and Moulton ([4]), analyzing analogous polarization curves obtained by them in chloric acid (from 0.5 to 9 M), believe that the transition to the upper, as they call it, Tafel straight line is caused by discharge of ClO_4^- ions with formation of the radical ClO_4. In the upper portion they distinguish two overvoltage regions with different mechanisms of oxygen evolution: the first region, immediately following the bend in the curve, in which decomposition of the radical ClO_4 is not yet observed, and oxygen is evolved through interaction of the radical with water according to the scheme

$$2ClO_4 + H_3O \rightarrow 2HClO + 2HClO_3 + \frac{3}{2}O_2$$

and the second region, beginning at currents approximately 10 times greater than those corresponding to the start of the bend in the curves, where chlorine dioxide is detected, formed during decomposition of the radical ClO_4, as indicated in works ([5], [6]).

In light of the results we obtained, such a conception of the mechanism of oxygen evolution seems not entirely correct. Indeed, analysis of the anolyte after electrolysis of 10 N perchloric acid, carried out at a current density corresponding to the beginning of the upper portion of the polarization curve, did not reveal the presence of either chlorine dioxide or the ClO_3^- ion, whereas the share of participation of the ClO_4^- ion in the process of oxygen evolution, according to mass-spectrometric data, reached 67%. Only at higher current densities ($3 \cdot 10^{-1}$ a/cm^2) did we also detect the appearance of chlorine dioxide in the anolyte and simultaneously observe an increase in the share of participation of the acid anion in oxygen evolution up to 78%.

Quantitative determination of chlorine dioxide in the anolyte was carried out iodometrically ([5]), and that of the chlorate ion by a colorimetric method (FEK-52 photoelectrocolorimeter) using the reaction with phenylanthranilic acid in a strongly sulfuric-acid medium, which makes it possible to determine the content of the ClO_3^- ion down to less than 0.005 mg/ml ([7]). In the case of electrolysis of more dilute perchloric acid solutions, a similar picture was observed, with the only difference that at current densities corresponding to the beginning of the upper portion of the curve, traces of the ClO_3^- ion were found, amounting to up to 0.2% of the share of participation of the acid anion, and the appearance of chlorine dioxide in the anolyte was detected at higher current densities than in the electrolysis of 10 *N* acid.

Table 1

Electrolyte	Overvoltage in V	Anodic current density in a/cm^2	O^{18} content in %	Enrichment in O^{18}, %	Share of acid anion participation, %
Ordinary water	–	–	0,198	0	–
Perchloric acid, 20°; 1 *N**	2,57	$6,0 \cdot 10^{-2}$	0,213	0,015	2,7
Perchloric acid, 20°; 1 *N*	2,95	$1,5 \cdot 10^{-1}$	0,216	0,018	3,3
Perchloric acid, 20°; 5,8 *N*	0,71	$5,2 \cdot 10^{-4}$	0,198	0	0
Perchloric acid, 20°; 5,8 *N*	1,62	$3,0 \cdot 10^{-2}$	0,216	0,018	3,3
Perchloric acid, 20°; 5,8 *N*	1,98	9,6	0,229	0,031	5,6
Perchloric acid, 20°; 7,6 *N*	0,74	$3,6 \cdot 10^{-4}$	0,198	0	0
Perchloric acid, 20°; 7,6 *N*	1,54	$4,0 \cdot 10^{-2}$	0,253	0,055	8,6
Perchloric acid, 20°; 7,6 *N*	1,70	$5,2 \cdot 10^{-1}$	0,317	0,119	18,6
Perchloric acid, 20°; 7,6 *N*	1,80	4,0	0,339	0,141	22,0

Electrolyte	Overvoltage in V	Anodic current density in a/cm^2	O^{18} content in %	Enrichment in O^{18}, %	Share of acid anion participation, %
Perchloric acid, 20°; 10 N	1,30	$4,3 \cdot 10^{-3}$	0,627	0,431	67,0
Perchloric acid, 20°; 10 N	1,55	$2,7 \cdot 10^{-1}$	0,697	0,499	78,0
Perchloric acid, 20°; 10 N	1,96	2,4	0,722	0,524	82,1
Perchloric acid, 20°; 10 N	4,25	5,3	0,723	0,525	82,3
Perchloric acid, –30°; 10 N	2,75	2,1	0,738	0,541	84,5
Perchloric acid, –30°; 10 N	4,25	4,25	0,743	0,546	85,3

* For the content of the heavy oxygen isotope in the initial perchloric acid solutions before electrolysis, see the footnote on p. 136.

These data give grounds to suppose that, up to the polarization at which chlorine dioxide is detected, despite the observed enrichment of oxygen with the isotope O^{18}, its evolution does not occur as a result of discharge of the ClO_4^- ion. The sharp increase in the electrode potential evidently leads to strong deformation of the adsorbed anions. Owing to this, conditions are created for an oxygen-exchange reaction between the adsorbed anion and the surface oxide of platinum, for enrichment of the evolved oxygen with the isotope O^{18}. Only at high current densities (from 10^{-1} a/cm^2 and above), at which an increase in the slope of the polarization curves is again observed, does partial discharge of the acid anion begin, accompanied by the formation of ClO_3^- ions in the anolyte and evolution of ClO_2.

It should be noted that the oxygen of the water distilled off from the acid after electrolysis had the ordinary isotopic composition, which indicates the absence of isotopic exchange between the products or intermediate products of electrolysis located on the electrode surface and water, and confirms the irreversibility of the electrochemical stage of formation of the surface oxide.

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Note: Figure translations are in progress. See original paper for figures.