from the anode compartment. It is interesting to note that the amount of lithium found from the current differs from that found by chemical analysis by a quantity which is constant over the entire region of the linear i vs φ dependence. This is an argument in support of chemical oxidation of the incorporated lithium, because it means that the rate of the competing process which depresses the current yield does not depend on potential, and this process, therefore, is a chemical rather than an electrochemical one.

Thus, the above investigation has shown that the chief characteristics of the process – its rate and mechanism – are independent of the state of aggregation of the cathode metal in the systems examined in the present work. But the anodic behavior of the intermetallic compounds may differ between solid and liquid electrodes, owing to side effects.

LITERATURE CITED

1. B. N. Kabanov, I. G. Kiseleva, I. I. Astakhov, and N. N. Tomashova, Élektrokhimiya, 1, 1023 (1965).
2. I. G. Kiseleva, B. N. Kabanov, and D. N. Machavariani, Élektrokhimiya, 6, 905 (1970).
3. I. I. Astakhov and B. N. Kabanov, Élektrokhimiya, 5, 749 (1969).
4. I. I. Astakhov, Élektrokhimiya, 8, 1549 (1972).
5. B. N. Kabanov, I. G. Kiseleva, I. I. Astakhov, N. N. Tomashova, and P. I. Petukhova, Élektrokhimiya, 10, 765 (1974).
6. S. P. Yatsenko, K. A. Chunzhonov, S. I. Alyanovskii, and É. N. Dieva, in: General Features in the Structure of Phase Diagrams of Metallic Systems [in Russian], Nauka, Moscow (1973), p. 56.
7. E. Zintl and G. Brauer, Z. Phys. Chem., B, 20, 245 (1933).
8. B. N. Kabanov, I. G. Kiseleva, I. I. Astakhov, and N. N. Tomashova, Élektrokhimiya, 1, 1023 (1965).
9. N. N. Tomashova, I. G. Kiseleva, and B. N. Kabanov, Élektrokhimiya, 7, 438 (1971).
10. N. N. Tomashova, I. G. Kiseleva, I. I. Astakhov, and B. N. Kabanov, Élektrokhimiya, 4, 471 (1968).

ADSORPTION OF IONS AND ELECTRIC DOUBLE-LAYER STRUCTURE ON TITANIUM – RUTHENIUM OXIDE ANODES

ADSORPTION OF SULFATE, CHLORIDE, AND PHOSPHATE IONS*

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UDC 541.13

The radiotracer technique was used to study the adsorption of sulfate, chloride, and phosphate ions on titanium–ruthenium oxide anodes as functions of potential and of anion concentration in the solution. Specific adsorption of the anions was shown to be present.

Titanium–ruthenium oxide anodes (TROA) presently are used in electrochemical chlorine production. Data on the adsorption properties and on electric double-layer structure on TROA are needed in order to elucidate the mechanism of this reaction. Such information is not available in the literature. In the present communication, experimental data are presented for the adsorption of sulfate, chloride, and phosphate ions on TROA as functions of potential and of anion concentration in the solution.

The TROA electrodes were titanium disks with an oxide layer consisting of 30% RuO_2 and 70% TiO_2 which had been applied to their lower surface by thermal decomposition of a mixture of titanium and ruthenium salts. The roughness factor of these electrodes was about 600.

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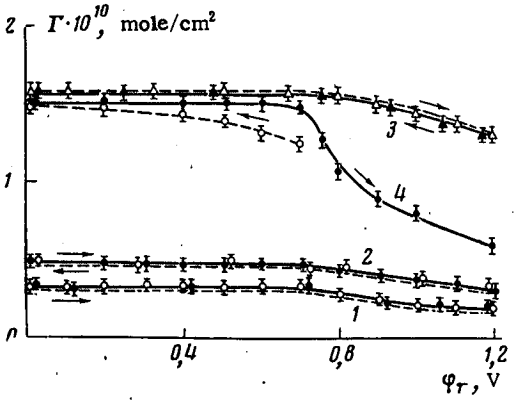

Fig. 1

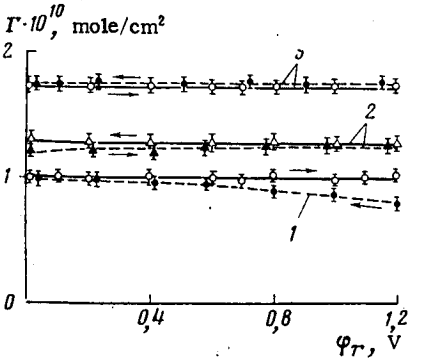

Fig. 2

Fig. 1. The adsorption of sulfate (1-3) and chloride (4) ions on TROA as a function of potential in solutions of the following composition: 1) 10^{-3} N H_2SO_4; 2) 10^{-3} N H_2SO_4 + 0.1 N $HClO_4$; 3) 10^{-1} N H_2SO_4; 4) 10^{-2} N NaCl + 0.1 N $HClO_4$. Arrows show the direction in which the TROA potential was changed.

Fig. 2. The adsorption of phosphate ions on TROA as a function of potential in solutions of the following composition: 1) 10^{-3} N H_3PO_4; 2) 10^{-3} N H_3PO_4 + 0.1 N $HClO_4$; 3) 10^{-2} N H_3PO_4.

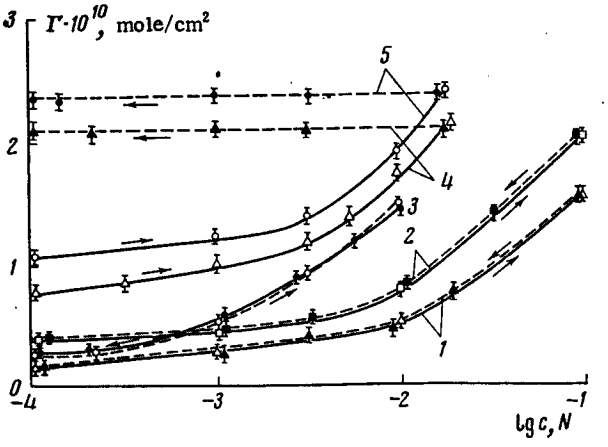

Fig. 3. The adsorption of sulfate (1, 2), chloride (3), and phosphate (4, 5) ions at 0.7 V as a function of their concentration in solutions of the following compositions: 1) xN H_2SO_4; 2) xN H_2SO_4 + 0.1 N $HClO_4$; 3) xN NaCl + 0.1 N $HClO_4$; 4) xN H_3PO_4; 5) xN H_3PO_4 + 0.1 N $HClO_4$. Arrows show the direction in which the concentration was changed.

The radiotracer technique [1] was used to examine the adsorption of the anions. Previously this technique had been widely used by us to study adsorption on platinum. The radioactive samples of sulfuric, phosphoric, and hydrochloric acid which were labeled with the corresponding isotopes ^{35}S, ^{32}P, and ^{36}Cl were subjected to additional purification at a platinum screen.

The experiments were done at 22°C. All solutions were prepared with twice distilled water; "os.ch." ["ultrapure"] grade perchloric acid was used as the base electrolyte, since it followed from preliminary data obtained by us that perchlorate ions have low adsorption activity on TROA.

Data on the adsorption kinetics of sulfate, chloride, and phosphate ions on TROA were obtained in the range of φ_r* between 0.0 and 1.2 V at anion concentrations in the solution of 10^{-3} to 10^{-2} N, either without base

* φ_r is the electrode potential relative to the reversible hydrogen electrode in the same solution.

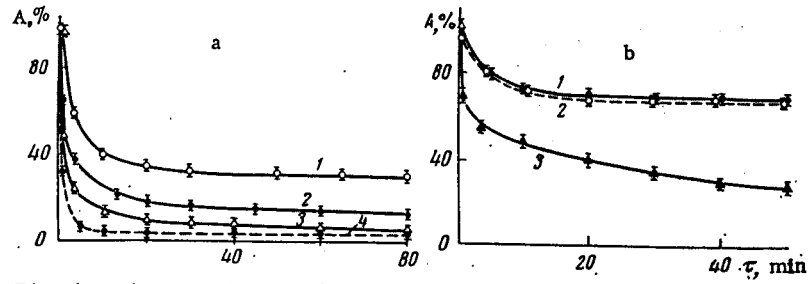

Fig. 4. Time variation of the amount of labeled, adsorbed sulfate (a) and phosphate (b) ions remaining on the electrode at a potential of 0.2 V in solutions of the following composition: a: 1) 0.1 N HCl, 2) 0.1 N $HClO_4$, 3) 10^{-3} N H_2SO_4 + 0.1 N $HClO_4$, 4) 10^{-2} N H_2SO_4 + 0.1 N $HClO_4$; b: 1) 0.1 N $HClO_4$, 2) 0.1 N HCl + 10^{-3} N H_2SO_4, 3) 0.1 N $HClO_4$ + 10^{-3} N H_3PO_4. Explanations in the text.

electrolyte or with 0.1 N $HClO_4$ as the base electrolyte. It was found that the time required to attain stationary adsorption values is less than 10 min when the concentration of the above anions in the solution was 10^{-3} N, and less than 2 min when the concentration was 10^{-2} N. The time required to attain stationary anion adsorption values is practically independent of the TROA potential.

The potential dependence of anion adsorption on TROA was measured over the range of φ_r from 0.0 to 1.2 V at different anion concentrations in the solution, both with and without base electrolyte. These measurements were done in the following way. When stationary anion adsorption had been attained at some value of potential in the range of φ_r between 0.0 and 1.2 V, then the electrode potential was displaced to a specified value of φ_r which differed from the previous value by 0.1 V; the electrode's radioactivity was measured periodically while a stationary adsorption value was attained at each φ_r. The data from these measurements are presented in Figs. 1 and 2, from which it can be seen that the starting potential of adsorption and the direction of potential change have no effect on the character of the Γ vs φ_r relations for sulfate ions, little effect in the case of phosphate ions, and a marked effect in the case of chloride ions. The anion adsorption is practically independent of φ_r over the range from 0.0 to 0.8 V (for phosphate ions from 0.0 to 1.2 V). The decrease in the adsorption of sulfate and chloride ions at $\varphi_r > 0.8$ V can be attributed to oxygen adsorption in this region of φ_r. It follows from Figs. 1 and 2 that increasing anion concentration in the solution (curves 1 and 3) and the presence of base electrolyte in the solution (curves 1 and 2) lead to higher anion adsorption over the entire range of φ_r studied.

Adsorption of the anions as function of their concentration in the electrolyte was measured over the range of φ_r from 0.2 to 0.7 V while varying the concentration of sulfate ions from 10^{-4} to 10^{-1} N, that of chloride ions from 10^{-4} to 10^{-2} N, and that of phosphate ions from 10^{-4} to $2 \cdot 10^{-2}$ N. Technically these measurements were performed as described in [2]. Data from these measurements which refer to 0.7 V are presented in Fig. 3. It follows from curves 1-3 of Fig. 3 that the dependence of sulfate and chloride ion adsorption on their concentration in the solution which was obtained when the concentration was changed from 10^{-4} to 10^{-1} (10^{-2}) N is completely the same as that obtained when the concentration was changed from 10^{-1} (10^{-2}) to 10^{-4} N. Complete desorption of the anions from the electrode surface is attained when the sulfate or chloride ion concentration in the solution is reduced practically to zero by replacing the adsorbate solution by base-electrolyte solution and maintaining the adsorbate concentration in the solution at a value close to zero by periodic replacement of portions of the base-electrolyte solution. One can assert on the basis of these data that the adsorption of said anions is reversible with respect to the adsorbate concentration in the solution.

It can be seen from curves 4 and 5 of Fig. 3 that the dependence of phosphate ion adsorption on their concentration in the solution which is obtained while increasing the adsorbate concentration in the solution (the solid sections of curves 4 and 5) is substantially different from that obtained while decreasing the adsorbate concentration (the dashed sections of curves 4 and 5). It also follows from curves 4 and 5 of Fig. 3 that after attainment of stationary anion adsorption from $2 \cdot 10^{-2}$ N adsorbate solution, a decrease in adsorbate concentration to 10^{-4} N is not attended by any change in the amount of adsorbed anions. Exposure of a TROA electrode which holds adsorbed phosphate ions to 0.1 N $HClO_4$ at $\varphi_r = 0.7$ V after 1 h leads to desorption of only 30-35% of the adsorbed anions. The above evidence points to strong, irreversible phosphate ion adsorption on TROA.

It follows from the data obtained that a change in electrode potential within the region of φ_r between 0.2 and 0.7 V has no effect on the concentration dependence of sulfate and phosphate ion adsorption, within the limits

of experimental error. It is seen by comparing curves 1 and 4 with curves 2 and 5 in Fig. 3 that the presence of base electrolyte in the solution causes an increase in sulfate and phosphate ion adsorption over the entire range of anion concentrations studied.

The kinetics of anion desorption from TROA in 0.1 N HCl or in 0.1 N $HClO_4$ and the kinetics of exchange between preadsorbed anions and anions of the same kind in the solution have been studied over the potential range from 0.2 to 0.7 V. Technically the measurements were done in the same way as described in [2]. That part of the data obtained in these measurements which pertains to φ_r = 0.2 V is presented in Fig. 4, where τ denotes the time of desorption or exchange, and A the amount (in %) of labeled, adsorbed anions remaining on the electrode. In all experiments for which results are presented in Fig. 4, anion adsorption was at 0.2 V from 10^{-3} N H_2SO_4 (or 10^{-3} N H_3PO_4) + 0.1 N $HClO_4$ solution. Curves 1 and 2 of Fig. 4 reflect the desorption kinetics of sulfate and phosphate ions; curves 3 and 4 of Fig. 4a and curve 3 of Fig. 4b reflect the exchange kinetics of adsorbed sulfate and phosphate ions, respectively.

It can be seen from Fig. 4 that desorption and exchange of adsorbed sulfate ions are faster than the corresponding processes involving phosphate ions (cf. curves 1 and 3 of Fig. 4a with curves 1 and 3 of Fig. 4b). Both for sulfate and phosphate ions, the exchange of adsorbed anions occurs more rapidly than their desorption (see curves 3 and 1 of Figs. 4a and b). Comparing curves 1 and 2 of Fig. 4a with curves 1 and 2 of Fig. 4b one can conclude that the desorption kinetics of sulfate ions depends on base-electrolyte composition, but that of phosphate ions does not. It can be seen by comparing curves 3 and 4 of Fig. 4a that the exchange rate of adsorbed sulfate ions increases with their concentration in the solution. A variation of electrode potential in the range of φ_r between 0.2 and 0.7 V has practically no effect on the desorption or exchange kinetics of sulfate and phosphate ions.

The data on the desorption kinetics of chloride ions (Cl^-) in 0.1 N $HClO_4$ and on the kinetics of exchange of these anions with ions of the same kind in the solution are not presented graphically, since these processes take place within times of less than 1 min, and cannot be studied quantitatively with the radiotracer technique used [1].

We have used the method of charging curves [3] to obtain additional information concerning the adsorption behavior of the anions on TROA. Anodic charging curves were measured over the potential range from 0.05 to 1.2 V using a current of 0.25 mA. Before starting the measurement the electrodes were held for 30 min at φ_r = 0.05 V. The measurements were carried out in 0.1 N $HClO_4$ containing sulfate and chloride ions at a concentration of 10^{-2} N, and in pure 0.1 N $HClO_4$. These measurements showed that the presence of significant quantities of adsorbed anions on the TROA surface (Fig. 3) causes very small alterations in the shape of the charging curves.

Thus, information concerning the adsorption behavior of anions on TROA has been obtained in the present work for the first time with a "direct" method (the radiotracer technique). The presence of specific adsorption of anions on TROA was demonstrated, and the principal features of these adsorption processes were studied.

It follows from the set of results presented above that a change in the potential drop across the electrode/solution interface in the case of TROA has no effect on the amount of adsorbed anions or their state on the surface. Experimental data obtained by other techniques are required to find the mechanism by which the potential drop across the solution/TROA electrode interface is generated.

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LITERATURE CITED

1. V. E. Kazarinov, Élektrokhimiya, 2, 1170 (1966); 8, 393 (1972).
2. V. E. Kazarinov and V. N. Andreev, Élektrokhimiya, 10, 196 (1974).
3. A. Shlygin and A. Frumkin, Acta Physicochim. URSS, 3, 791 (1935).