SOME PECULIARITIES OF THE BEHAVIOR OF PALLADIUM, RUTHENIUM, AND PALLADIUM-RUTHENIUM ELECTRODES IN SOLUTIONS OF ORGANIC SUBSTANCES

(UDC 541.135.52-44)

V. S. Éntina, O. A. Petrii, and I. V. Shelepin

M. V. Lomonosov Moscow State University

Translated from Élektrokhimiya, Vol. 2, No. 4,
pp. 457-464, April, 1966
Original article submitted July 5, 1965

The high activity of electrolytically mixed deposits of palladium and ruthenium (20-27% ruthenium) in the oxidation of methanol was demonstrated. The following activity series of electrodes were obtained in the electrooxidation of HCOOH and $HCOO^-$: Pd ≫ Pt + Ru > Pt > Pd + Ru ≫ Ru and Pd + Ru > Pd > Pt + Ru > Pt > Ru, respectively. Hypotheses were advanced on the nature of the effects of acceleration of reactions on mixed catalysts and the mechanism of the processes of electrooxidation. The charging curves on electrolytically mixed deposits of palladium and ruthenium and the potentiostatic curves on a ruthenium plated electrode were measured and discussed.

In [1], the high catalytic activity of electrolytically mixed precipitates (EMP) of platinum and ruthenium in the electrooxidation of methanol was demonstrated. It was subsequently found that the electrooxidation of methanol also proceeds at a higher rate on EMP of palladium and ruthenium than the components of the deposit. Analogous effects for alloys of platinum and palladium with ruthenium have been described by Bockris and Wroblowa [2].

The purpose of this work was to study the behavior of EMP of palladium and ruthenium in solutions of organic substances. For comparison we also performed some measurements on palladium-plated, ruthenium-plated, and platinum-ruthenium (9:1) electrodes.

MEASUREMENT PROCEDURE

The measurement procedure was described in [3, 4]. The EMP of palladium and ruthenium were deposited upon a platinum plate (2 cm^2) from a solution of 1% ($PdCl_2$ + $K_2RuNOCl_5$) at a current density of 6 mA/cm^2. Their compositions were determined with the aid of Ru^{106} [5]. Palladium plating was conducted from 1% $PdCl_2$, acidified with HCl, at a current density of 6 mA/cm^2. In contrast to [1], in which a solution of $K_2RuNOCl_5$ was used for ruthenium plating, in this work the electrode was ruthenium plated in 0.1 N KOH, with simultaneous solution of the metallic ruthenium powder on the anode [6]. The current density was 2-4 mA/cm^2. Black, rather strongly retained precipitates are obtained in this case. As has been shown in [6], the ruthenium electrodes thus obtained prove more active in reactions of electroreduction of a number of organic substances than those precipitated from nitrosochloride solutions.*

Before the experiment, in an individual vessel, the palladium-ruthenium and ruthenium electrodes were subjected to cathode polarization in sulfuric acid solution, while the palladium-plated and platinum-ruthenium electrodes were subjected to anode polarization, and then (after replacement of the electrolyte) cathode polarization at a current density of 10-20 mA/cm^2.

The experiments were conducted at room temperature, 20 ± 2° C. The potentials φ_r are cited with respect to the reversible hydrogen electrode in the same solution.

---

*We had noted that on ruthenium precipitates obtained by various methods, the charging curves differ somewhat in shape, especially in the oxygen region.

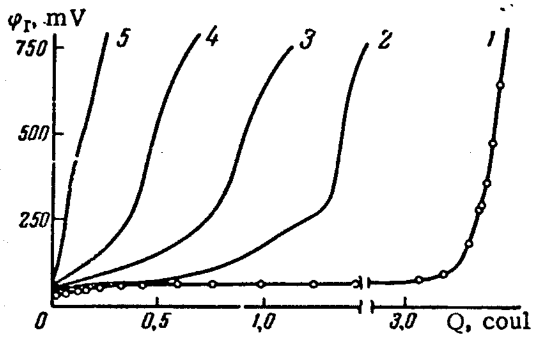

Fig. 1

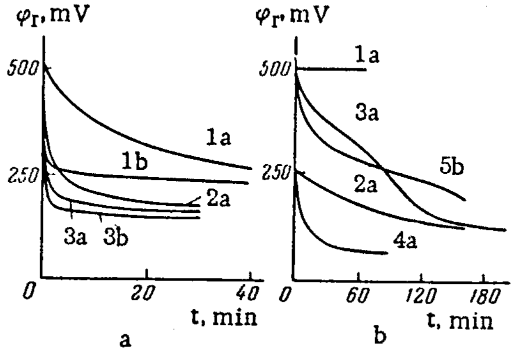

Fig. 2

Fig. 1. Anodic charging curves on palladium-plated (1) and palladium-ruthenium electrodes, containing 7%(2), 20% (3), and 27% (4)ruthenium and on a ruthenium electrode (5) in 1N H_2SO_4. Current density in the measurement of the charging curves: 1) $5 \cdot 10^{-4}$, 2) $3 \cdot 10^{-4}$, 3) $2 \cdot 10^{-4}$, 4) $1.5 \cdot 10^{-4}$, 5) 10^{-4} A/cm^2.

Fig. 2. Potential shifts upon the introduction of methanol into contact: A) with palladium-plated (1a and 1b), platinum-plated (2a), and palladium-ruthenium (3:1) (3a and 3b) electrodes (CH_3OH concentration 0.1 M); B) with ruthenium-plated electrode at a methanol concentration of 0.5 M (1a, 2a) and 3M (3a, 4a, 5b). The index a pertains to 1N H_2SO_4 and the index b to 1N KOH.

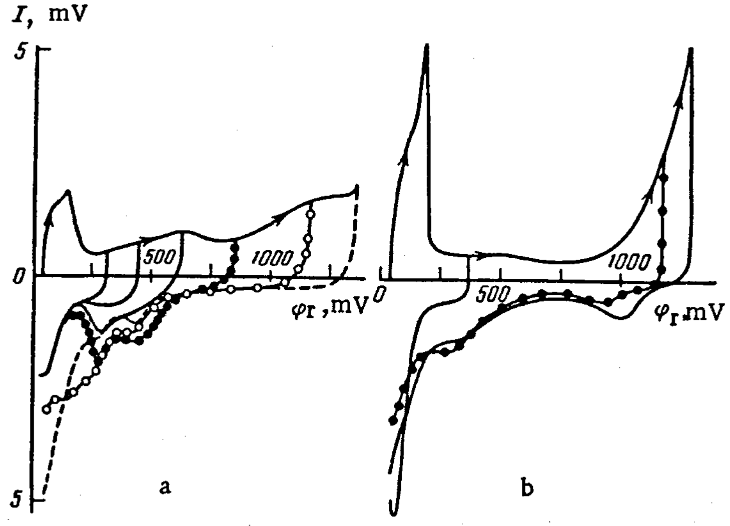

Fig. 3. Potentiostatic curves of a ruthenium electrode in 1N H_2SO_4 (a) and in 1N KOH (b). Rate of development 11 mV/sec.

EXPERIMENTAL RESULTS AND THEIR DISCUSSION

We prepared palladium-ruthenium electrodes containing 7, 20, and 27% ruthenium by weight. The charging curves, measured on these electrodes in 1N H_2SO_4, are shown in Fig. 1 in comparison with the charging curves on palladium and ruthenium.

When ruthenium is introduced into the electrolytic precipitate, the length of the hydrogen portion of the charging curve, i. e., the amount of sorbed hydrogen, is reduced; however, dissolution of hydrogen in the EMP of palladium and ruthenium evidently occurs even at a ruthenium content of 27%. The horizontal portion, characteristic of the phase transition on a palladium electrode [7], disappears on the mixed precipitates and at a ruthenium content of 7%, the potential over the entire extent of the charging curve already depends upon the amount of electricity passed through. An interesting peculiarity of the charging curves on palladium-ruthenium electrodes is their more sloping shape in the region of potentials 350-750 mV in comparison with the palladium electrode. An analogous phenomenon is also observed on platinum-ruthenium electrodes [1] and is evidently due to the earlier oxidation of the electrode surface in the presence of ruthenium in the deposit.

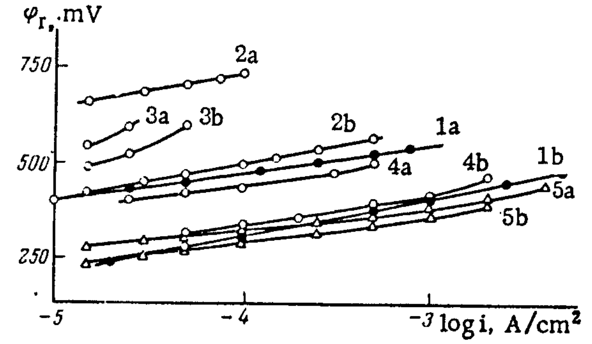

Fig. 4. Stationary polarization curves of the electrooxidation of methanol in 1N H_2SO_4 (a) and 1N KOH (b) on various metals; 1) platinum-plated electrode (0.5 M CH_3OH), 2) palladium-plated electrode (0.1 M CH_3OH), 3) ruthenium-plated electrode (3M CH_3OH); 4) palladium-ruthenium electrode (3:1) (0.1 M CH_3OH), 5) palladium-ruthenium electrode (0.5 M CH_3OH).

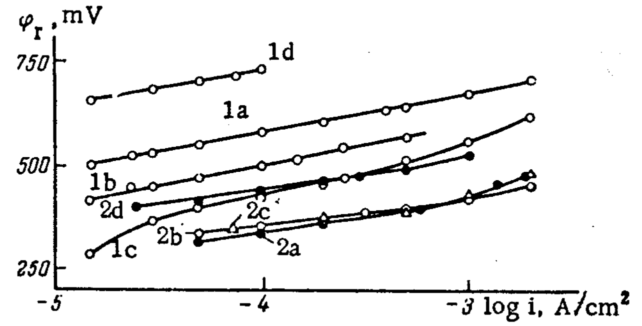

Fig. 5. Dependence of the rate of oxidation of methanol (0.1 M) on the pH on Pd (1) and Pd + Ru (2) in solutions of 0.1 N KOH (a), 1 N KOH (b), 6 N KOH (c), 1 N H_2SO_4 (d).

Measurements of the curves of the potential shift after the introduction of methanol into contact with the electrodes, stationary polarization curves, and curves of the electrooxidation of the chemisorbed products indicate that the highest rates of oxidation of methanol are observed at ruthenium contents in the precipitate from 20 to 27%. Subsequently the basic measurements were conducted on electrodes possessing the indicated composition.

Figure 2 compares the curves of the shift of the potential upon the introduction of methanol into contact with the investigated electrodes. Although a shift of φ_r only in the cathodic direction is observed in all cases, the nature of the curves and the potentials established are greatly dependent upon the nature of the electrode. From the curves of the shift of φ_r and measurements of the charging curves [8, 4], it may be concluded that the rate of dehydrogenation of methanol on a free surface or a surface little covered by a chemisorbed substance [4, 8, 9] is higher in the case of a palladium-ruthenium electrode than in the case of a palladium-plated electrode. On a palladium-plated electrode in acid solutions, methanol is oxidized only at a low rate. In alkaline solution, the rate of dehydrogenation of methanol increases, while still remaining lower than on a palladium-ruthenium catalyst. On ruthenium, as was shown in [1] for electrodes prepared by a different method, after the introduction of 0.5 M CH_3OH at 500 mV, practically no shift of φ_r is observed. A shift of φ_r occurs at an appreciable rate only when the methanol concentration is increased to 3M. The curves obtained in this case are similar to the curves of the shift in φ_r of a Pt/Pt electrode in those cases when the organic substance is placed in contact with an oxidized electrode [10, 11]. After the placement of CH_3OH in contact with a ruthenium-plated electrode, polarized to a potential of 250 mV, a gradual shift of the potential in the cathodic direction can be observed in the presence of 0.5 M and 3M CH_3OH, which takes the same form as in the case of other investigated electrodes. After long periods of time, φ_r reaches values close to the reversible hydrogen potential. The peculiarities of the behavior of ruthenium noted above are caused by early oxidation of its surface [6, 1] and by properties of the oxides that arise.

The results of a study of the adsorption of hydrogen and oxygen on a ruthenium-plated electrode by a potentiostatic method are shown in Fig. 3. According to these measurements, the deposition of oxygen on the ruthenium surface begins at low anode potentials. The oxides formed are reduced at φ_r close to the beginning of the deposition of hydrogen. When the final φ_r of the development in acid solutions is increased to a definite value, the strength of the oxides increases so much that the regions of their reduction and of the deposition of hydrogen merge. The maxima on the anodic curve and the maxima and plateaus on the cathodic curve in acid solutions are evidently related to the presence of different forms of adsorbed oxygen. In alkaline solutions, the maximum ionization of adsorbed hydrogen is substantially higher than in acid, which corresponds to a greater amount of adsorbed hydrogen. The nature of the deposition and removal of adsorbed oxygen and its amounts in alkali are different from those in acid; however, oxidation of the surface, just as before, begins early, and the oxides formed possess a greater energy of the bond to the surface. The increase in the current on the potentiostatic curves at the extreme anodic potentials is due to dissolution of ruthenium, which occurs simultaneously with the formation of the oxide layer. After the polarization of ruthenium in alkali up to the potentials of dissolution, a maximum appears on the cathodic curve in the region from 1.2 to 0.8 V, the height of which is greater, the higher the potential of the change in the direction of the development. We did not determine the nature of this maximum.

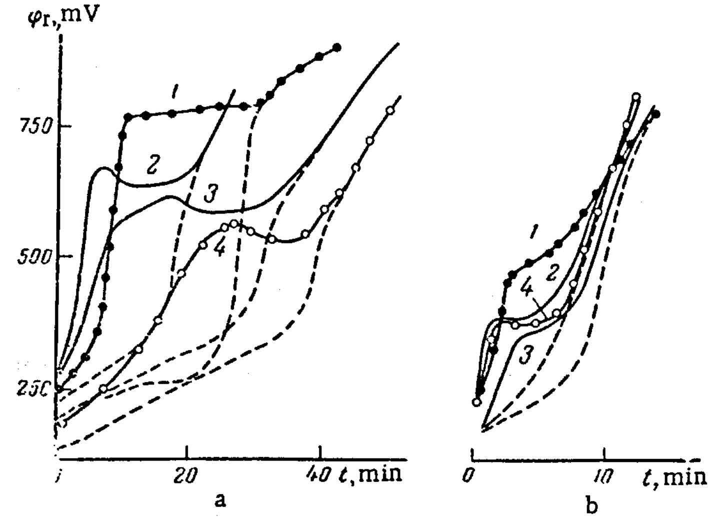

Fig. 6. Curves of the electrooxidation of substances chemisorbed in the polarization of palladium-plated (a) and palladium-ruthenium (b) electrodes in 1N H_2SO_4 (1), 0.1 N KOH (2), 1N KOH (3) and 6N KOH (4). Dotted lines—anodic charging curves. Current density: a) $5 \cdot 10^{-5}$, b) $1.5 \cdot 10^{-4}$ A/cm^2.

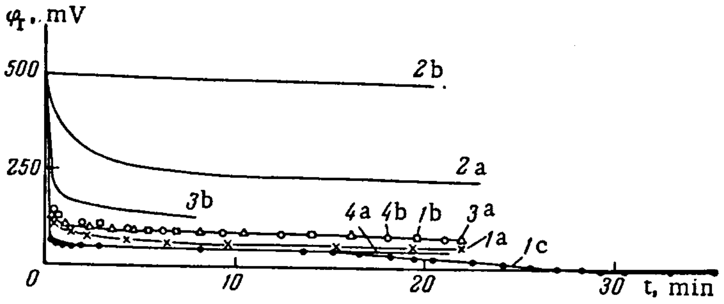

Fig. 7. Curves of the shift of the potential of palladium-plated (1), ruthenium-plated (2), platinum-ruthenium (3), and palladium-ruthenium (4) electrodes in solutions of formic acid and sodium formate: a) 1N H_2SO_4 + 0.1 M HCOOH, b) 1N KOH + 0.1 M HCOONa, c) 1 N H_2SO_4 + 5 M HCOOH.

The electrodes studied are arranged in approximately the same series with respect to rate of electrooxidation of methanol under stationary conditions as that indicated above for the oxidation reaction at the first moment after introduction of the substance. Although no determination was made of the true surfaces of the catalysts, this does not appreciably hinder the comparison of the results, since the differences in activity are so small that they cannot be explained by a different value of the electrode surface.

On a ruthenium-plated electrode (Fig. 4), the oxidation of methanol at a stationary rate begins to be observed only at low current densities and high concentrations of the substance. When the current density is increased, there is a passivation of the electrooxidation process. The electrooxidation of methanol also occurs with large overvoltage in acid solutions on a palladium-plated electrode. The slope of the polarization curve on palladium is equal to ~ 95-100 mV.

As we pass to a palladium-ruthenium electrode in acid solution, the decrease in the overvoltage is ~ 250 mV in comparison with the palladium-plated electrode; the slope of the polarization curve is ~ 65-75 mV. The rate of electrooxidation of methanol on this electrode is higher than on palladium-plated platinum; however, it is lower than on platinum-ruthenium, which possesses the highest activity in acid solutions. Thus, the introduction of ruthenium

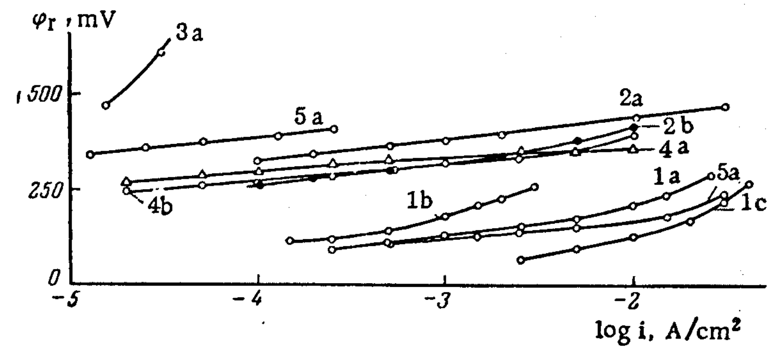

Fig. 8. Stationary polarization curves of the electrodeposition of HCOOH in 1N H_2SO_4 (a) and of HCOONa in 1N KOH (b) on palladium-plated (1), platinum-plated (2), ruthenium-plated (3), platinum-ruthenium (4), and palladium-ruthenium (5) electrodes. The concentration of HCOOH and HCOONa equals 0.1 M for curves 1 (a and b); 3.5 and 0.5 M–2.4 and 5M for curve 1c.

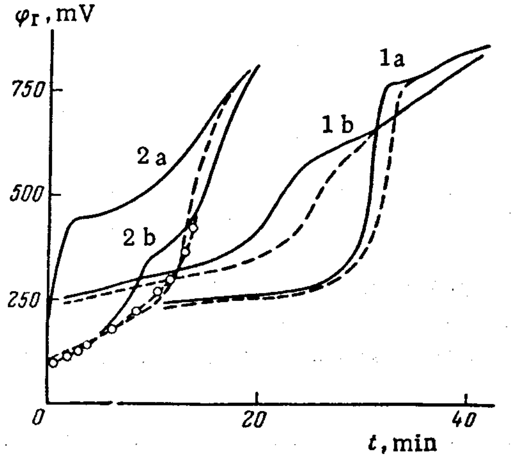

Fig. 9. Curves of the electrodeposition of the products of chemisorption of HCOOH (a) and HCOONa (b) on palladium-plated (1) and palladium-ruthenium (2) electrodes in 1N H_2SO_4 and 1N KOH. Dotted line–anodic charging curves in background solutions. Current density: 1a and 1b–$5 \cdot 10^{-5}$; 2a and 2b–$1.5 \cdot 10^{-5}$ A/cm².

into the deposit causes a substantial improvement of the catalytic properties of platinum and palladium in the electrodeposition of methanol.

As it follows from the data obtained (Fig. 4), in alkaline solutions the overvoltage of the electrooxidation of methanol is usually lower than in acid solutions. However, the acceleration of the process by alkalies differs on different electrodes. It reaches the greatest value on palladium-plated and platinum-plated electrodes, while on a platinum-ruthenium electrode the shift of the overvoltage upon passage from 1N H_2SO_4 to 6N KOH is only 30-50 mV. The analogy in the behavior of palladium and platinum is also manifested in the fact that in alkaline solutions, with increasing pH the overvoltage decreases, while passivation of the process begins at lower current densities (Fig. 5) [4]. Evidently on palladium, just as was assumed for platinum in [4], the mechanism of the process in alkaline solutions changes.

On EMP of palladium and ruthenium, the rate of electrooxidation of methanol is higher in alkaline solutions than in acid solutions. However, the effect is not so great as on palladium, and a change of the pH of the medium to alkaline has no influence upon the reaction rate. Such a phenomenon may be explained if we assume that in alkaline solutions the nature of the organic residue participating in the rate-determining step changes, for example, as a result of its interaction with OH^- ions [4]; moreover, this transition is accomplished at pH < 13. The latter means that the particle participating in the slow step of the process is not the initial methanol molecule, the pK of which is close to 16 [12].

The results of a measurement of the curves of the electrodeposition of chemisorbed products (Fig. 3) agree with the conclusions on the activity of the investigated electrodes in the reaction of electrooxidation of methanol under stationary conditions. In this case, in the transition to mixed catalysts, a strong decrease in the overvoltage, corresponding to the shift of the stationary polarization curves, is also observed. For the investigated electrodes, just as for platinized platinum [9, 4], in a first approximation it is correct that the process of electrooxidation of methanol under stationary conditions is determined by removal of the chemisorption products from the electrode surface.

The nature of the curves of oxidation of chemisorption products depends greatly upon the nature of the electrode. In alkaline solutions on a palladium-plated electrode, these curves have a complex form. The maxima on the curves are observed not only at the beginning of the retention, but also after oxidation of part of the chemisorbed substance. The same phenomena are also observed on a Pt-Pt electrode [4]. The dependence of the overvoltage of the oxidation of chemisorbed products upon the degree of coating on the palladium-ruthenium electrode is simpler. In this case, usually the overvoltage of the process increases with decreasing coverage. Only in concentrated alkali, is a small maximum observed before the oxidation plateau. In this respect, the EMP of palladium and ruthenium behave analogously to platinum-ruthenium catalysts [1].

From the data obtained it follows that a similarity is observed in the principles of the oxidation of methanol on palladium-plated and platinum-plated electrodes on the one hand, and on platinum-ruthenium and palladium-ruthenium electrodes, on the other. The processes in the second case obey simpler kinetic principles. In particular, this pertains to the influence of the pH of the medium upon the reaction rate and to the nature of the curves of electrooxidation of the chemisorption products. The slight dependence of the overvoltage of electrooxidation of methanol upon the pH may be the result of the fact that on mixed catalysts, both in acid and in alkaline solutions, the slow step of the process is the interaction of chemisorption products with the OH radicals [4]. In accord with this, the slope of the polarization curves on mixed catalysts is close to 60 mV. Transferring the concept of the oxidation of methanol by OH radicals to mixed catalysts, the increase in the rate of the process should be explained by a decrease in the strength of the bond of the chemisorption products to the electrode surface as a result of a change in the nature of the electrode. For a further investigation of the properties of mixed catalysts, we conducted experiments with formic acid analogous to those described above.

As is well known, formic acid decomposes at a great rate on the surface of a palladium electrode, saturating it with hydrogen [13]. After the introduction of HCOOH into contact with the palladium electrode, stabilized at φ_r ~500 mV, the potential is rapidly shifted into the region of φ_r of the phase transition (Fig. 7). In a concentrated solution of HCOOH, values of φ_r more negative than the reversible hydrogen potential are reached, and in this case the evolution of gaseous hydrogen is observed.

As was first noted by A. G. Polyak*, the evolution of gases also occurs at the initial stage of the potential drop. We performed no analysis of the gases. According to the data of Polyak, these gases contain appreciable amounts of hydrogen. The evolution of hydrogen in solutions of HCOOH at φ_r more positive than the reversible hydrogen potential has been described and discussed in [14] for platinized platinum. On a palladium-ruthenium electrode, the shifts of the potential in the negative direction in the presence of HCOOH are approximately the same as on a palladium-plated electrode. From the curves of the potential shift, we can conclude that the activity of ruthenium is low in the dehydrogenation of formic acid and the formate ion.

The results of a measurement of the stationary polarization curves in solutions of HCOOH on various electrodes are cited in Fig. 8. In acid solutions, the highest rate of oxidation of HCOOH is observed on a palladium-plated electrode, which also agrees with measurements of the curves of the potential shift. As we pass to a palladium-ruthenium electrode, there is a great increase in the overvoltage of the process. On a platinum-ruthenium electrode, the rate of electrooxidation of HCOOH is somewhat higher than on platinized platinum, but substantially lower than on a palladium-plated electrode. Thus, in spite of the fact that shifts of φ_r in acid solutions occur at a great rate on platinum-ruthenium and palladium-ruthenium electrodes and reach low values of the potential, the rate of oxidation under stationary conditions is comparatively low.

In an alkaline solution of formate, higher rates of oxidation are achieved on a palladium-ruthenium electrode as a result of the fact that in this case passivation of the process occurs at higher current densities than on a palladium-plated electrode. On a ruthenium electrode in alkaline solutions of formate, a stationary state is not established.

Thus, the electrodes studied are arranged in the following sequence with respect to activity in the reaction of electrooxidation of formic acid: Pd > Pt + Ru > Pd + Ru ≫ Ru and in the electrooxidation of the formate ion: Pd + Ru > Pd > Pt + Ru ≫ Ru. A comparison of the curves of the electrooxidation of chemisorption products of formic acid on various electrodes leads to interesting conclusions. Only small quantities of chemisorption products are accumulated on a palladium-plated electrode (Fig. 9); moreover, the rate of oxidation is very low, just as for the chemisorption products of methanol. The overvoltage of the process in alkaline solution is lower than in acid solution. The oxidation potentials of the chemisorbed products are substantially higher than the overvoltages in the presence of HCOOH in solution at the same current densities. On a palladium-ruthenium electrode, in comparison with palladium, the rate of oxidation of the chemisorption products is greatly increased. In acid solution, the amount of chemisorption products also increases at the same time (Fig. 9). Although in acid solution the rate of

---

*Personal communication.

oxidation of the chemisorption products is approximately equal to the rate of the reaction under stationary conditions, in alkaline solution this ratio is not fulfilled. On a platinum-ruthenium electrode, both in acid and in alkaline solutions, a great increase in the rate of oxidation of chemisorbed HCOOH and $HCOO^-$ is observed in comparison with the platinum electrode, while the galvanostatic curves are similar to the curves of the electrooxidation of chemisorbed methanol. The overvoltages of the oxidation of the chemisorption products and of the process in the presence of organic substances in solution are close.

Thus, on mixed catalysts the electrooxidation of chemisorbed HCOOH and $HCOO^-$ occurs at higher rates than on the components of the deposit. However, this does not lead in all cases to an acceleration of the process under stationary conditions. The ratio between the transition state of the reaction in the case of oxidation of chemisorbed substances and in the presence of the reacting compound in the volume of the solution is more complex for HCOOH and $HCOO^-$ than for CH_3OH [14]. On Pt + Ru and Pd + Ru in acid, the hypothesis that the reaction is determined by removal of the chemisorption products is fulfilled. Such a hypothesis is not correct for Pt [14], Pd, and Pd + Ru in alkali.

The low overvoltages of the electrooxidation of HCOOH and $HCOO^-$ on palladium and of $HCOO^-$ on palladium-ruthenium electrodes, as well as the presence even of negligible amounts of chemisorbed products when the reaction occurs under stationary conditions in these cases permits us to assume that the electrooxidation of HCOOH and $HCOO^-$ occurs according to a mechanism of dehydrogenation; moreover, a strong dependence of the rate of dehydrogenation upon the electrode potential is observed. Thus, the slope of the straight line 1a (Fig. 8) on the initial portion is ~ 60-70 mV. It may be that such a slope of the curve is associated with appreciable coating of the palladium surface with adsorbed hydrogen within the investigated potential region. A decrease in the slope of the polarization curve of the dehydrogenation of methanol on a Pt electrode in the case of large coverages of the surface with hydrogen was detected in [4]. In acid solution on a palladium-ruthenium electrode, chemisorption products accumulate, which leads to a change in the limiting step of the process. Under stationary conditions, evidently the process is determined by interaction of the chemisorption products with OH radicals.

We would like to thank Academician A. N. Frumkin for his participation in the discussion of the experimental results.

LITERATURE CITED

1. O. A. Petrii, Dokl. AN SSSR, 160, 871 (1965).
2. J. O'M. Bockris and H. Wroblowa, J. Electroanalyt. Chem., 7, 428 (1964).
3. A. N. Frumkin and B. I. Podlovchenko, Dokl. AN SSSR, 150, 349 (1963).
4. O. A. Petrii, B. I. Podlovchenko, and A. N. Frumkin, Khira Lal, J. Electroanalyt. Chem. No. 10, 253 (1965).
5. O. A. Petrii and V. E. Kazarinov, Élektrokhimiya, 1 1389 (1965).
6. G. P. Khomchenko, T. N. Stoyanovskaya, and G. D. Vovchenko, Vestn. Mosk. Univ., Ser. Khim., No. 5, 30 (1962); No. 2, 20 (1963); T. N Stoyanovskaya, Dissertation [in Russian], Moscow State University (1964).
7. A.N. Frumkin, and N. Aladzhalova, Zh. Fiz. Khimii, 18, 493 (1944); A. N. Frumkin and A. I. Fedorova, Zh. Fiz. Khimii, 27, 247 (1953).
8. B. I. Podlovchenko, O. A. Petrii, and E. G. Gorgonova, Élektrokhimiya, 1, 182 (1965).
9. Khira Lal, O. A. Petrii, and B. I. Podlovchenko, Élektrokhimiya, 1, 316 (1965).
10. G. A. Bogdanovskii, Dissertation [in Russian], Moscow State University (1959).
11. J. E. Oxley, G. K. Johnson, and B. T. Buzalsky, Electrochim. Acta, 9, 897 (1964); G. Bianchi and P. Longhi, Chimica e l'industrie, 46, 1280 (1964).
12. P. Ballinger and F. A. Long, J. Amer. Chem. Soc., 82, 795 (1960).
13. N. Nylen, Z. Électrochem., 43, 915 (1937).
14. B. I. Podlovchenko, O. A. Petrii, and A. N. Frumkin, Khira Lal, J. Electroanalyt. Chem., 11, 12 (1966).