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PROMOTION WITH ADATOMS AND MICRODEPOSITS OF CATALYSTS USED IN ELECTROCHEMICAL ENERGETICS SYSTEMS^{*)}

By

Yu. B. VASSILIEV^{**)}

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Abstract

Studies have been made of the influence of various adatoms and microdeposits on relatively inert supports upon the kinetics and mechanism of different electrochemical reactions. It is shown that the catalytic effect depends primarily on the mechanism of the electrochemical reaction. For one reaction adatom can act as promoter and for another as poison. Generally the action of promoter (or poison) is to change the surface concentration or the strength of the bond with the surface of one of reacting particles. Adsorbed cation and adatom are two extreme cases of one phenomenon.

The transition from adatoms to microcrystals has been studied. It is shown that with decreasing cluster size on support, the specific catalytic activity of a single atom in a cluster can both increase (Pt, Ir, Rh on GC and Ti) and decrease (Pd on GC) or remain unaffected (Pd on Nb). With increasing cluster on support gradually approaches that in monolithic metal.

In recent years much attention has been given in electrochemical energetics to micropromotion with adatoms and microdeposits as one of the most important ways of increasing drastically the catalytic activity and decreasing expenditure of precious metals.^{1~10)} Deposition of monolayers and submonolayers of foreign metals is a relatively simple means of modifying the electrocatalytic properties of the surface and also a convenient method for investigation of surface effects in electrocatalysis.¹¹⁾

Adsorption of monolayers and submonolayers of foreign metals at potentials more positive than the thermodynamic potential of their deposition can lead to a change in the electronic and adsorption properties of the surface,^{12~14)} probably, due to strong interaction of valence orbitals of adsorbed species with electron gas of the metal, which in its turn should lead to a sharp

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change in the catalytic properties.¹⁵⁾ As shown by our studies, these sub-molecular layers are layers of chemisorbed cations, which have partly or completely lost their charge. Specific adsorption of inorganic cations on platinum and platinum group metals has been the subject of numerous studies both by means of the charging or potentiodynamic curves and by the radioactive tracer method.¹²⁾

The dependence of the surface coverage by various cations on potential shows that the potential range in which adsorbed cations exist on the surface depends both on the cation and the electrocatalyst nature. As can be seen from Fig. 1, when passing from zinc to tin cations and further to mercury cations, the potential range and which adsorbed cations exist on the surface widens considerably. Zinc cations are completely desorbed from the platinum electrode surface already at the potential 0.4 V and thus it is clear why they do not affect the methanol electrooxidation process on platinum, which

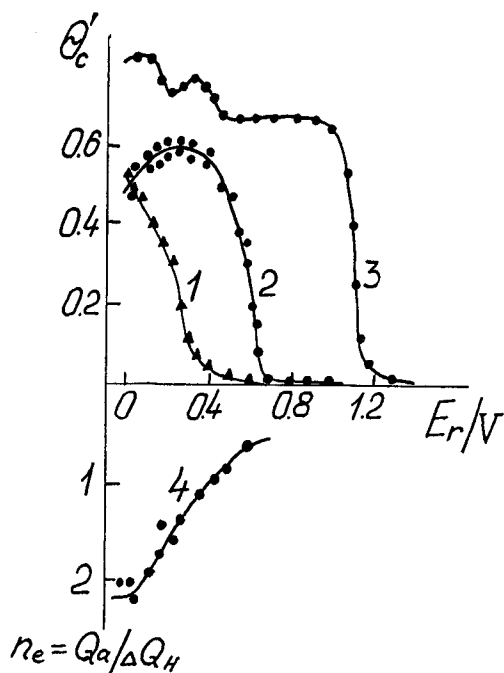


Fig. 1. Dependence on E_r of the platinum surface coverage with zinc (1), tin (2) and mercury (3) cations and the relation $Q_{ox}/\Delta Q_H$ for tin ions (4). $1 \cdot 5 \cdot 10^{-3} M$ $ZnSO_4 + 0.5 M$ H_2SO_4 $2.4 \cdot 5 \cdot 10^{-5} M$ $SnSO_4 + 0.5 M$ H_2SO_4 $3 \cdot 10^{-4} M$ $Hg(NO_3)_2 + 0.5 M$ H_2SO_4 .

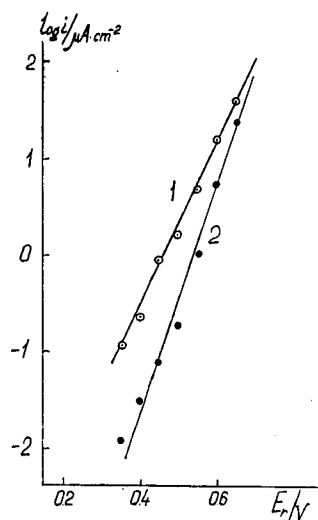


Fig. 2. Polarization curves of methanol electrooxidation on platinumized platinum in $1 M$ H_2SO_4 in the absence of tin (2) and after tin adsorption on the surface from $5 \cdot 10^{-4} M$ $SnSO_4$ (1).

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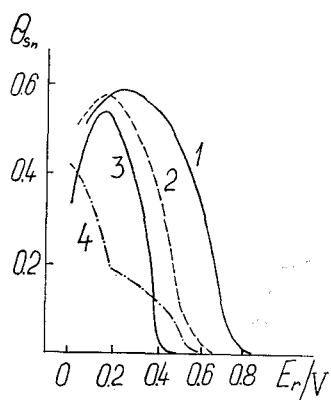


Fig. 3. Dependence on E_r of the platinum (1), iridium (2), palladium (3) and rhodium (4) surface coverage with tin cations in 10^{-2} M $\text{SnSO}_4 + 0.5$ M H_2SO_4 .

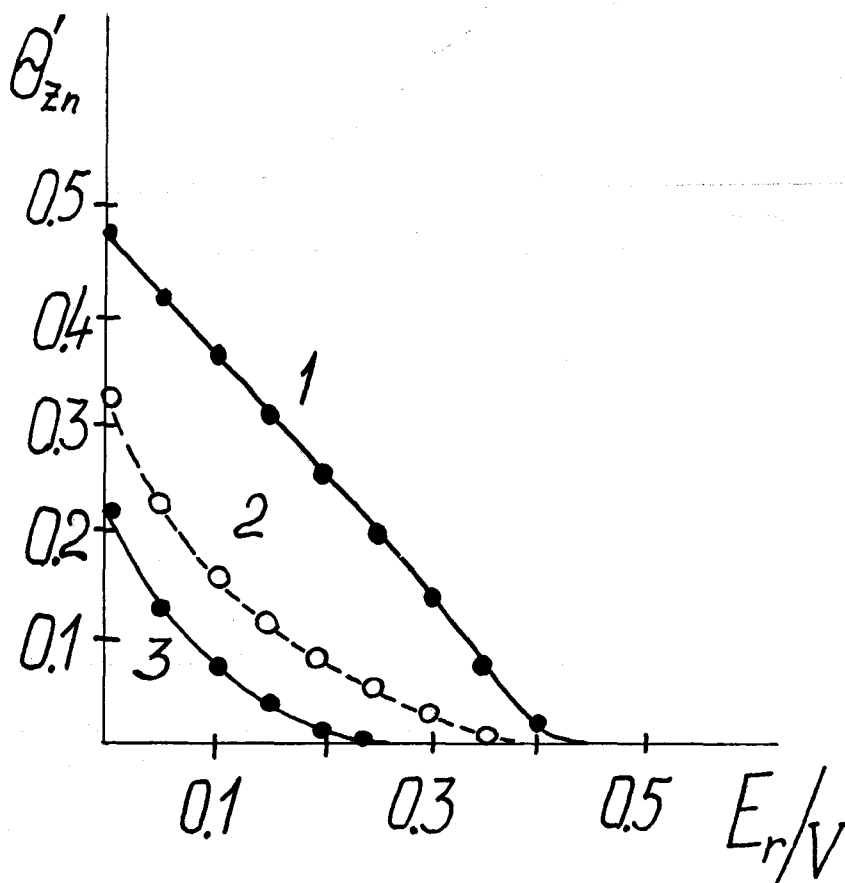


Fig. 4. Dependence on E_r of the platinum (1), iridium (2) and rhodium (3) surface coverage with zinc cations in $5 \cdot 10^{-3}$ M $\text{ZnSO}_4 + 0.5$ M H_2SO_4 .

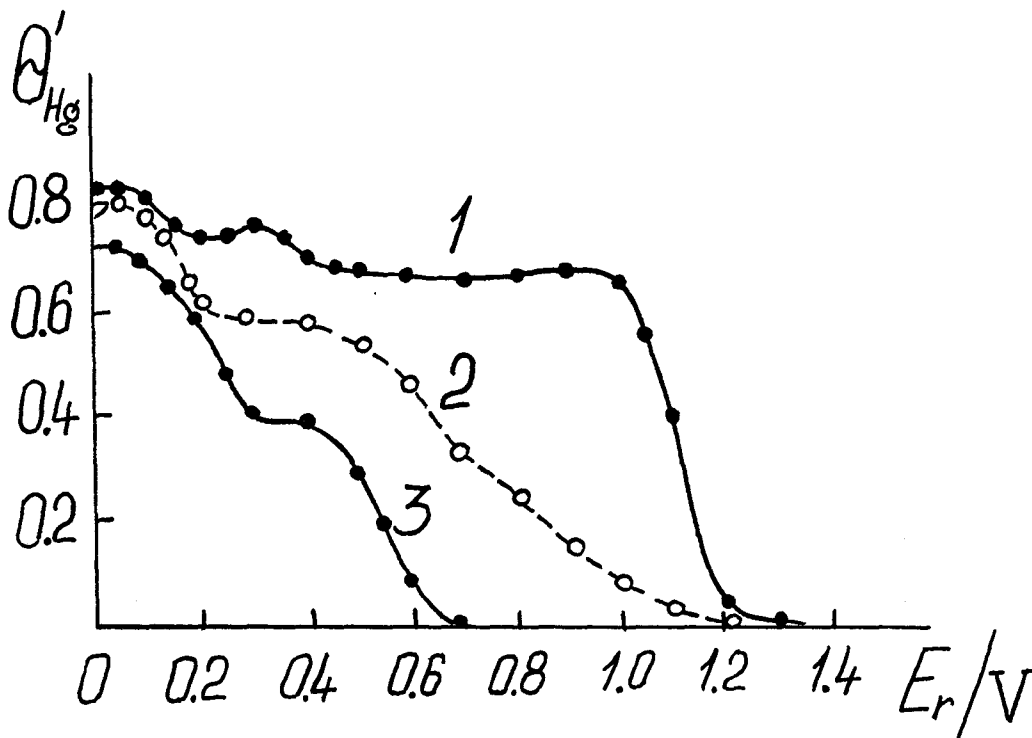


Fig. 5. Dependence on E_r of the platinum (1), iridium (2) and rhodium (3) surface coverage with mercury cations in 10^{-4} M $\text{Hg}(\text{NO}_3)_2 + 0.5$ M H_2SO_4 .

occurs in the potential range from 0.4 to 1.0 V. As can be seen from Fig. 2 tin drastically accelerates methanol electrooxidation in the potential range up to 0.7 V, whereas mercury hinders this process up to 1.2 V. When passing from platinum to iridium, palladium and rhodium, the adsorption region of one and the same cation narrows down sharply (Fig. 3~5). On a rhodium electrode the electrode surface is free of tin already at the potential 0.4 V (Fig. 3). Hence it is clear why on rhodium tin has no effect on methanol electrooxidation though on platinum it strongly accelerates this reaction.

It has been found that adsorption of alkali and alkali-earth metal cations does not involve any appreciable charge transfer from surface to cation and adsorbed cation is present on the surface as a charged particle. In this case due to strong mutual repulsion between adsorbed cations, the factor in the kinetic and steady-state adsorption isotherms increases strongly.¹⁶⁾

Adsorption of other cations, however, involves complete or partial charge transfer. Thus in the course of tin adsorption on platinum on the anodic

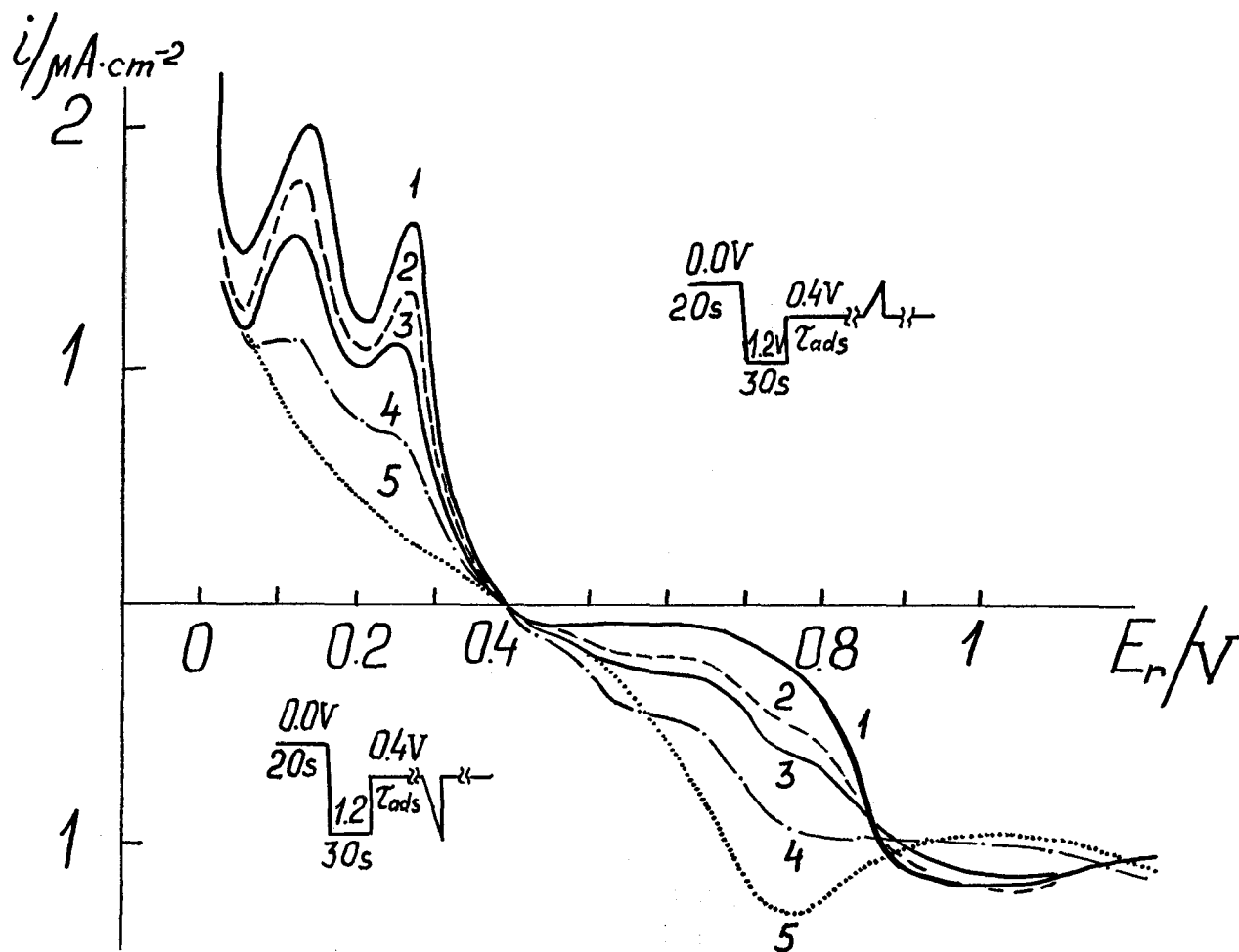


Fig. 6. Cathodic and anodic $i-E_r$ curves for smooth platinum at $E_F^{\text{init}}=0.4\text{ V}$ in $0.5\text{ M H}_2\text{SO}_4$ (1) and in the presence of $5\cdot 10^{-5}\text{ M SnSO}_4$ for various τ_{ads} : 2- 10, 3- 20, 4-50, 5-300 s.

potentiodynamic curve there appear and increase maxima of adsorbed tin oxidation (Fig. 6). From the ratio of the amount of electricity consumed in oxidation of chemisorbed tin Q_{ox} to decrease in the amount of adsorbed hydrogen in the presence of tin ions ΔQ_H , it is possible to determine the number of electrons donated to the electrode when chemisorbed tin is removed, occupying one adsorption site: $n = Q_{ox}/\Delta Q_H$.⁹ In the potential range $0 \sim 0.2$ V $n=2$, *i. e.*, on platinum surface tin is present as a neutral adatom Sn^0 . At $E_n > 0.2$ V, however, $n < 2$, *i. e.*, we have to do with partial charge transfer. In this case with increasing anodic potential value, the apparent effective charge of adsorbed tin increases (Fig. 1). The presence of the charge on chemisorbed tin particles at $E_r = 0.6$ V is evidenced by enhanced value of f in the adsorption isotherm (Fig. 7) caused by forces of mutual repulsion of charged chemisorbed particles. Increase in the degree of "the ionic state" of the platinum bond with cation with increasing anodic potential value is also observed for other cations (Fig. 8).¹⁷ Already on passing from platinum to iridium the potential range in which tin exists on the surface as neutral adatoms drastically narrows down.

The results obtained by us show that adsorbed cation and adatom are two extreme cases of one phenomenon. In the case of tin adsorption on iridium first there occurs hydrogen redistribution along the energy bonds, *i. e.* the species in question is adsorbed as cation and only later the amount of adsorbed hydrogen decreases and maxima appear on the anodic poten-

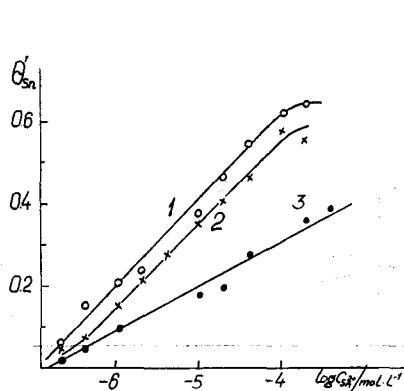


Fig. 7. Dependence of the steady-state platinum surface coverage with tin ions on their bulk concentration in 0.5 M H_2SO_4 at various adsorption potentials: 1-0.2, 2-0.4, 3-0.6 V.

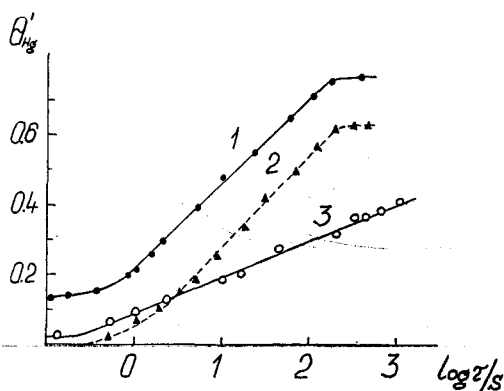


Fig. 8. Dependence of the platinum surface coverage with mercury cations on the adsorption time in 10^{-4} M $Hg(NO_3)_2 + 0.5$ M H_2SO_4 at various adsorption potentials: 1-0.2, 2-0.4, 3-0.8 V.

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tiodynamic curves the species turns into an adatom strengthening its bond with the surface and losing the charge (Fig. 9). Thus the adsorbed state of a modifying additive on the electrode surface depends both on the time of its presence on the surface and on the electrode potential. The state of the promoting additive on the electrode surface to a large degree defines the nature of its influence on the electrocatalytic properties of the electrode. Comparison of adsorption and polarization data shows that at first tin adsorption does not affect hydrogen overvoltage but with time this increases at a practically constant value of surface coverage by tin (Fig. 10) due to increasing charge transfer and to strengthening of the bond between adatom and substrate. Thus along with the surface coverage by adatom, we should take into consideration the degree of "the ionic state" and the strength of the bond of adatom with the electrode surface.¹⁸⁾

One of the most important factors to be taken into account

when considering the promoting action of adatoms is the influence of adsorbed cations on the adsorption of various species on the surface, including the reacting ones. Adsorption of cations affects strongly the extent and energetics of hydrogen and oxygen adsorption on a catalyst. Since adsorbed hydrogen and oxygen are intermediate species playing an enormous role in many reduction and oxidation processes, adsorption of cations should exert a significant

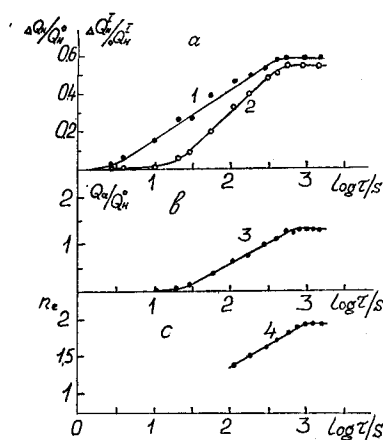


Fig. 9. Dependence of $\Delta Q_H^I/Q_H^I$ (1), $\Delta Q_H^I/Q_H$ (2), Q_{ox}/Q_H (3) and $n = Q_{ox}/\Delta Q_H$ (4) for tin cations adsorption on the iridium electrode in 10^{-2} M $\text{SnSO}_4 + 0.5 \text{H}_2\text{SO}_4$ at $E_{ads} = 0.1$ V on the adsorption time.

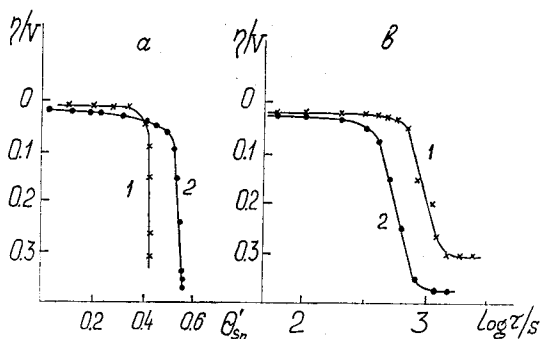


Fig. 10. Dependence of hydrogen overvoltage at $i = 5 \cdot 10^3 \text{ A} \cdot \text{m}^{-2}$ on iridium on the adsorption time (a) and surface coverage with tin cations (b) in $0.5 \text{M H}_2\text{SO}_4 + 10^{-2} \text{M SnSO}_4$ at $E_{ads} = 0.025$ V (1) and $E_{ads} = 0.1$ V (2).

influence on these processes.⁹⁾

Most frequently a base, or less noble, promoting element in a binary system favours oxygen adsorption. Tin has a promoting effect on electro-oxidation of methanol, formic acid and other organic substances in the potential range 0.2~0.6 V, when tin is present on the surface as SnOH, *i. e.* serves as sites for absorption of OH_{ads}. In the potential range under consideration the slow step of the oxidation processes is interaction of adsorbed organic species with the radicals OH_{ads} formed in the preceding fast electrochemical step of the discharge of water molecules:



It is possible to draw unambiguous conclusions about the mechanism of acceleration of the electrooxidation processes of simple organic substances on platinum in the presence of promoters only if quantitative account is taken of the influence of promoter on the adsorption of organic substance and oxygen and on the basis of direct comparison of polarization and adsorption measurements.

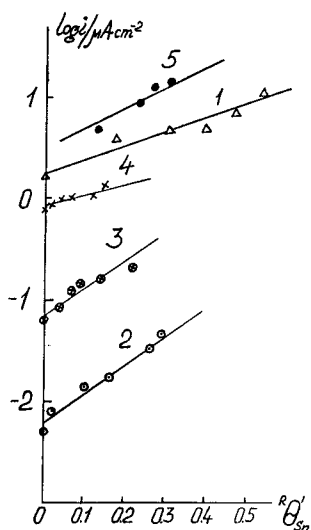


Fig. 11. Dependence of electrooxidation rate on the surface coverage with tin ions for smooth platinum in 0.1 M HCOOH + 0.5 M H₂SO₄ solution at $E=0.4$ V (1) for platinized platinum in 0.1 M CH₃OH + 0.5 M H₂SO₄ solution at $E=0.4$ V (2), 0.1 M HCOOH + 0.5 M H₂SO₄ at 0.3 V (3) and at 0.4 V (4); for platinized platinum at constant coverage with respect to tin, (5) 0.4 V, 0.1 M HCOOH.

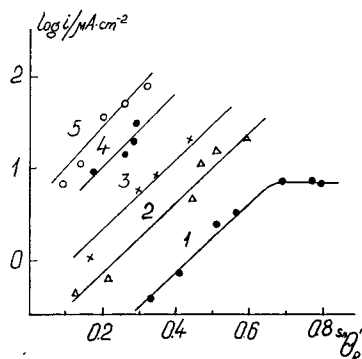


Fig. 12. Dependence of HCOOH electrooxidation current for platinized platinum at constant surface coverage with tin ions on the surface coverage with organic species. The values of θ'_{Sn} : 1-0, 2-0.13, 3-0.24, 4-0.31, 5-0.54.

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It follows from Fig. 11 that at constant potential and organic substance concentration in solution the rate of oxidation of methanol and formic acid both on smooth and platinum electrodes increases exponentially with increasing tin surface concentration θ'_{Sn}

$$i = K \cdot \exp(\lambda \cdot \theta'_{Sn}) \quad (2)$$

The rate of oxidation increases in spite of the fact that with increasing extent of adsorption of tin, the surface coverage by the particles undergoing oxidation decreases. This indicates that the accelerating effect on the electrooxidation process is much greater than the hindering effect, associated with decrease of adsorption of organic substance undergoing oxidation.

In order to elucidate the true catalytic effect of tin in electrooxidation of organic substances it is necessary to compare the rates at constant surface coverage by organic substance.

Fig. 12 shows the dependences of the rate of electrooxidation of formic acid on a platinized platinum electrode at different surface coverages by tin on the surface concentration of formic acid. It is clear from the figure that the rate of electrooxidation of formic acid rises exponentially with increasing surface coverage by chemisorbed particles

$$i = K_{\theta_{Sn}} \cdot \exp(\beta_1 \cdot f \cdot \theta'_{Sn}) \quad (3)$$

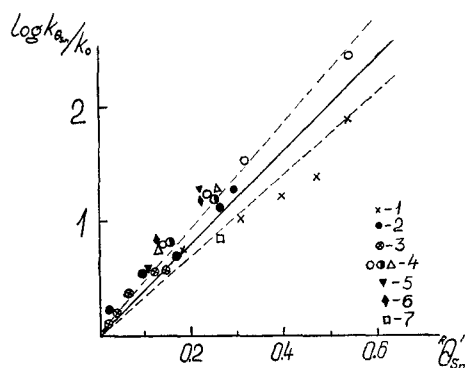


Fig. 13. Dependence of the oxidation rate of organic substances on the surface coverage with tin ions at $E=0.4$ V, at $\theta_R=\text{const}$ for: smooth platinum in 0.1 M HCOOH + 0.5 M H₂SO₄ solution (1), platinized platinum: 0.1 M CH₃OH + 0.5 M H₂SO₄ (2), 0.1 M HCOOH + 0.5 M H₂SO₄ (3), platinized platinum at constant coverage with respect to tin (4), for chemisorbed species from HCOOH on smooth platinum electrodes: $E_P^{\text{ox}}=0.6$ V (5), $E_P^{\text{ox}}=0.65$ (6) and from CH₃OH on platinized platinum electrode: $E_P^{\text{ox}}=0.65$ V after washing electrode (7).

In this case when passing from an untreated platinized electrode to electrodes promoted with different amounts of tin, the nature of dependence does not change. As can be seen from Fig. 13, the promoting effect of tin seems to consist in a sharp increase of the constant in Equation (3)

$$K_{\theta_{\text{Sn}}} = K_0 \cdot \exp(\beta_2 \cdot f \cdot R \theta'_{\text{Sn}}) \quad (4)$$

where $\beta_2 f = 10$.

On platinum adsorbed tin accelerated not only the oxidation of organic substance when it is present in solution bulk, but also the electrooxidation of prechemisorbed substances. Fig. 14 gives the $i-\tau$ oxidation curves of particles prechemisorbed from 1 N CH_3OH solution at $E_r = 0.3 \text{ V}$ in 0.5 M H_2SO_4 at $\theta'_{\text{Sn}} = 0$ (Curve 1) and $\theta'_{\text{Sn}} = 0.27$ (Curve 2).

Platinum is a very good adsorbent with respect to methanol and formic acid and ensures a sufficiently high surface coverage by the species being oxidized, but the coverage of platinum surface by the radicals OH_{ads} in this potential range is slow. In this potential range tin is prone to adsorb oxygen easily and therefore it can be assumed that the adsorbed tin atoms are the sites on which occurs enhanced adsorption of OH_{ads} participating in the oxidation process.

The obtained experimental data show that the nature of the effect of tin on the rate of the electrochemical process on platinum is determined by the mechanism of this process and the influence of tin on the adsorption of reacting species. When passing from platinum to iridium at the same potential we have a higher OH_{ads} concentration and therefore tin additions lead to a much less acceleration of methanol oxidation on iridium (Fig. 15).

Earlier we showed that formic acid electrooxidation on palladium follows a mechanism different from that on platinum.¹⁹⁾ Experimental data indicate that tin adsorption on palladium hinders drastically electrooxidation of formic acid on a palladium electrode, *i. e.* in this case tin is poison (Fig. 16). Tin also acts as poison for other reactions in which OH_{ads} do not participate —

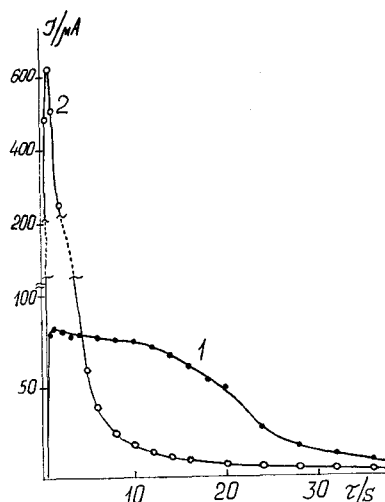


Fig. 14. Oxidation rate of species (chemisorbed from 1 M $\text{CH}_3\text{OH} + 0.5 \text{ M H}_2\text{SO}_4$ at $E_r^{\text{ads}} = 0.3 \text{ V}$) in the background solution at $E_r^{\text{ads}} = 0.65 \text{ V}$: 1 — $\theta'_{\text{Sn}} = 0$, 2 — $\theta'_{\text{Sn}} = 0.27$ after rinsing the platinum electrode with this solution.

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for hydrogen evolution and ionization, maleic acid electroreduction and some others.

It is interesting to note that experiments with a rotating disk electrode from a platinum-tin alloy with the surface continuously renewed by scouring with a diamond cutter showed that on commercial platinum-tin alloys no drastic acceleration of the electrooxidation of simple organic substances is observed as compared with a platinum electrode. This indicated that formation of an alloy changes the manner different from that observed

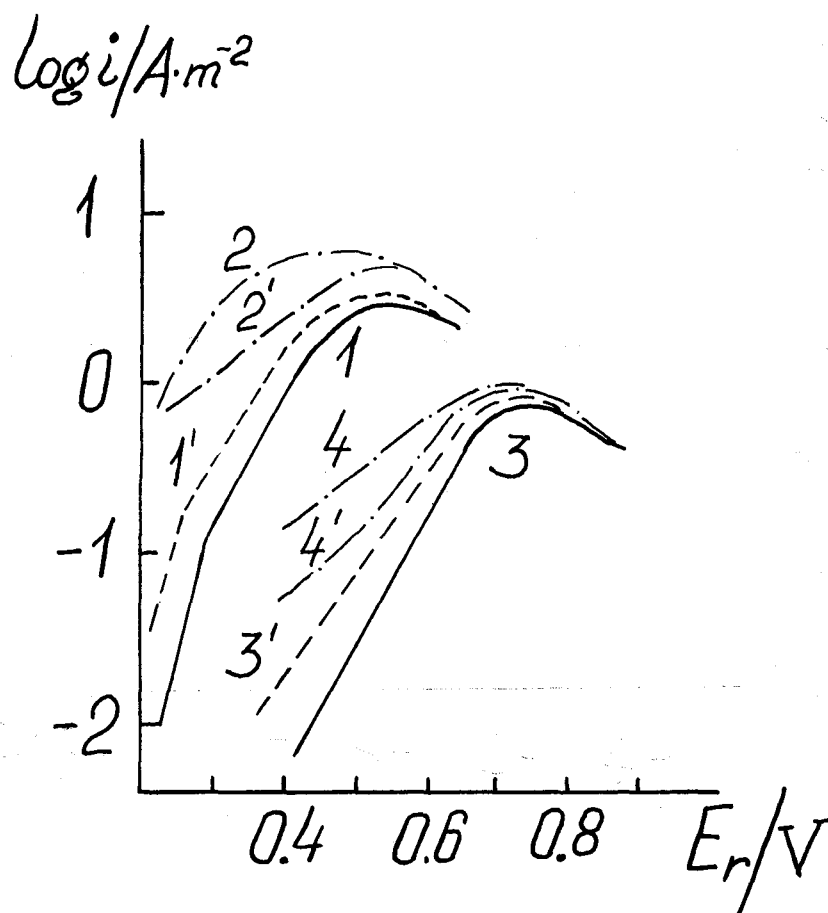


Fig. 15. Polarization curves of formic acid and methanol electrooxidation on iridium in 1 M $\text{CH}_3\text{OH} + 0.5 \text{ M H}_2\text{SO}_4$ (3, 4) and 1 M $\text{CH}_3\text{OH} + 0.5 \text{ M H}_2\text{SO}_4 + 10^{-2} \text{ M SnSO}_4$ (3', 4'), in 1 M $\text{HCOOH} + 0.5 \text{ M H}_2\text{SO}_4$ (1, 2) and $+10^{-2} \text{ M SnSO}_4$ (1', 2'). The maximal non-steady current (2, 2'; 4, 4') and the steady current (1, 1'; 3, 3').

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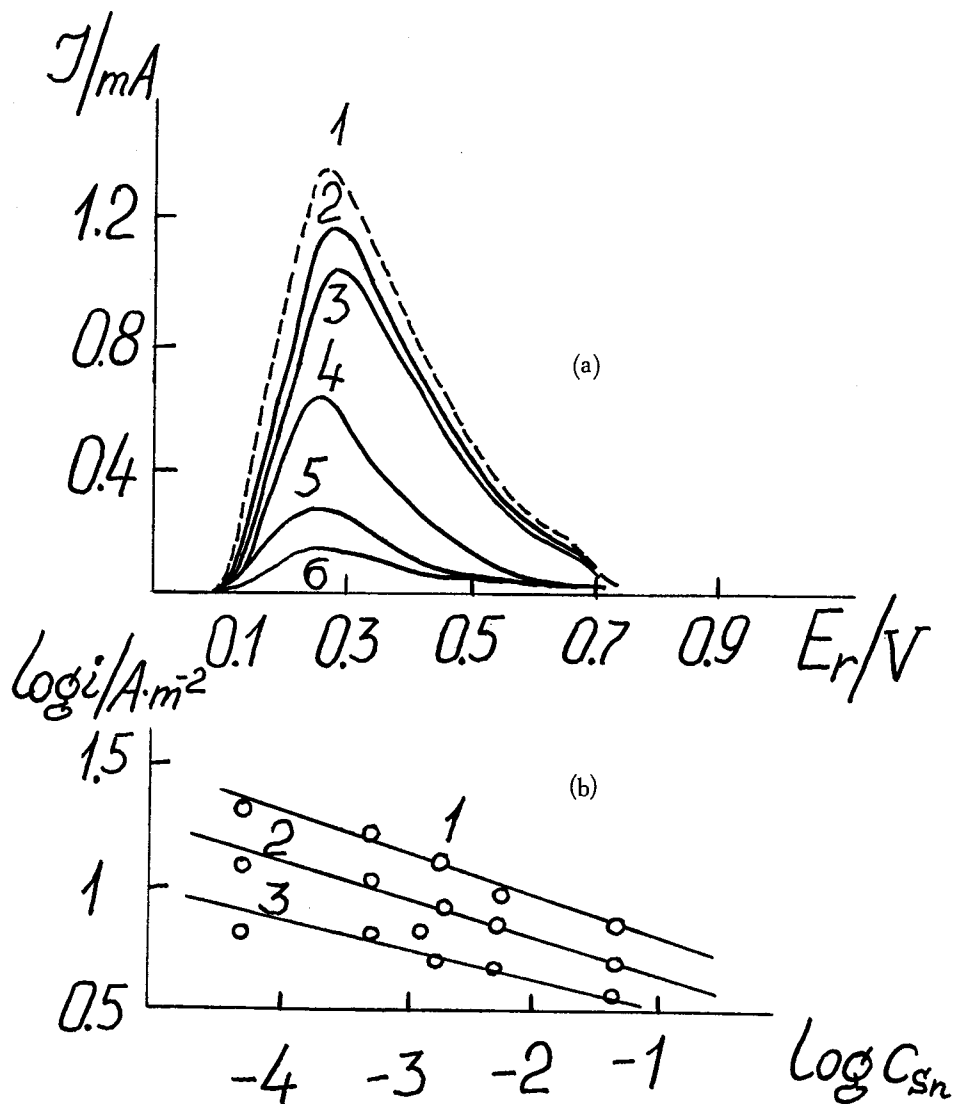


Fig. 16. Polarization curves of formic acid electrooxidation on palladium in 1 M $\text{HCOOH} + 0.5 \text{ M H}_2\text{SO}_4$ in the presence of SnSO_4 : 1-0, 2- $5 \cdot 10^{-5} \text{ M}$, 3- $5 \cdot 10^{-4} \text{ M}$, 4- $2 \cdot 10^{-3} \text{ M}$, 5- $5 \cdot 10^{-3} \text{ M}$, 6- 10^{-2} M (a) and dependence of electrooxidation rate on the bulk concentration of SnSO_4 at various adsorption potentials: 1-0.25 V, 2-0.2 V, 3-0.15 V (b).

during the formation of an adatom of one metal on the surface of another. For this reason it is necessary to take into account the influence of the adatom-substrate bond on the adsorption properties of the adatom itself.

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Thus the influence of a promoting component on the electrocatalytic activity to a large degree depends on the nature of the electrode catalyst, the mechanism of the reaction occurring on it, the nature and state on the surface of the promoter itself, the adsorption on the surface of reacting and foreign substances and their competition with the promoting component for the catalyst surface. In the case of an electron-transfer reaction without significant adsorption of reacting substances the influence of adatoms is very slight (the influence on the processes in the system quinone/hydroquinone and $\text{Fe}^{+2}/\text{Fe}^{+3}$). The conclusion about the promoting effect of adatom on redox systems drawn by Adzic R. R. and Despic A. R.²¹⁾ is erroneous and can be explained by the fact that they did not differentiate between the adatoms formed before the thermodynamic potential is reached and the microcrystals formed at higher potential values. Skundin and Tuseeva²²⁾ studied the influence of silver on the processes in the redox system $\text{Fe}^{+2}/\text{Fe}^{+3}$ on a gold electrode. The concentration of silver Ag^+ varied from 2, 5 to 2500 mole/l. Depending on the number of silver ions, the equilibrium potential of the system Ag^+/Ag was either more negative or more positive than that of the system $\text{Fe}^{+2}/\text{Fe}^{+3}$. If it was more positive silver was present as adatoms, if more negative, silver microcrystals were formed on gold. As can be seen from Fig. 17, as the surface coverage of gold by silver adatoms increases, the exchange current decreases slightly, at potentials close to the equilibrium potential of the system Ag^+/Ag at which a phase of silver microcrystals is formed, the electrode working surface increases and the exchange current grows. But this is an entirely new different phenomenon-micropromotion by microcrystals.

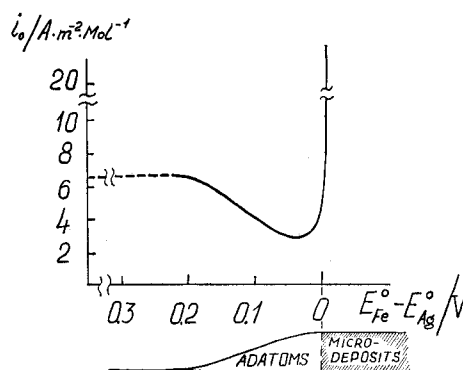


Fig. 17. Dependence of the exchange current of the system $\text{Fe}^{+2}/\text{Fe}^{+3}$ on $E_{\text{Fe}^{+2}/\text{Fe}^{+3}}^{\circ} - E_{\text{Ag}^{+}/\text{Ag}}^{\circ}$.

Of particular interest is micropromotion of inert electrodes-carriers with microcrystals of catalytically active metals. We studied the adsorption and electrocatalytic properties of platinum, iridium, rhodium, palladium and ruthenium microdeposits on titanium as an inert carrier, as well as platinum microdeposits on various inert carriers: glass, carbon, pyrographite, gold, titanium, niobium, etc. In many cases the adsorption and electrocatalytic

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properties of microcrystals were studied after introduction into solution of a metal-catalyst salt by measuring from the very first moment the appearance of nuclei and their growth to microcrystals of different size. In what follows all specific catalytic activity values given are referred to the relative surface of microdeposits with respect to the carrier surface (S_c/S_s), which varied with

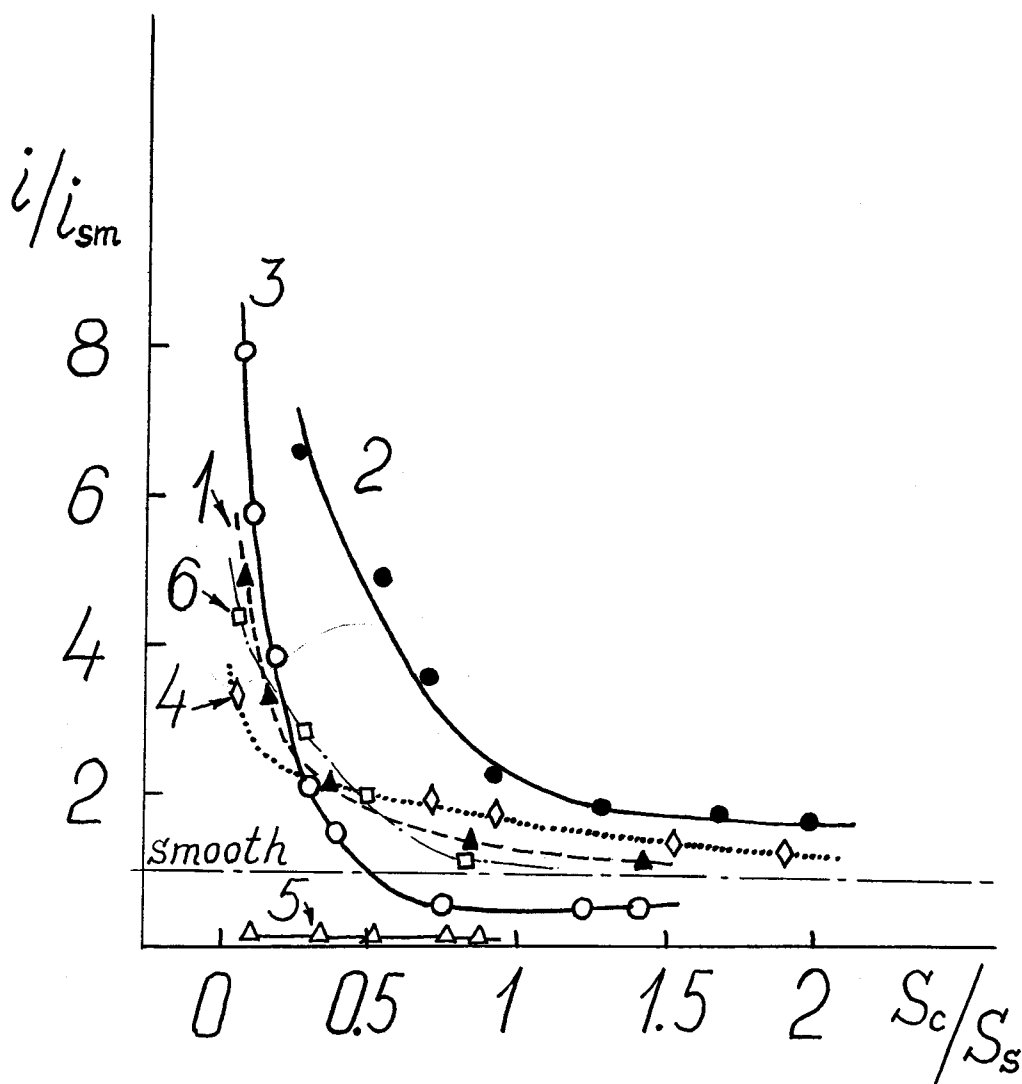


Fig. 18. Dependence of the relative of hydrogen evolution on the relative surface of microdeposits of platinum metals with respect to the titanium surface: 1-Pt, 2-Ir, 3-Rh, 4-Pd, 5-Ru, 6-Os.

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the deposition time. As shown by the studies by means of a scanning electron microscope, on the carriers used by us, characterized by a high over-voltage of the generation of metal-catalyst nuclei they start to grow with time and practically no new nuclei appear. Therefore the ratio S_c/S_s is proportional to the mean size of the catalyst crystallite or cluster on the carrier surface.

As can be seen from Fig. 18, the specific rate of the hydrogen evolution reaction per atom in small platinum, iridium and rhodium clusters differs from that per massive catalyst atom, exceeding it by almost an order of magnitude. These effects are pronounced on platinum, iridium and rhodium and practically absent on palladium. With increasing mean cluster size, the specific rate of hydrogen evolution decreases, gradually approaching that on a massive catalyst. Analysis of the energy spectra of hydrogen adsorption shows that on small cluster the energy of the hydrogen bond with catalyst is less than the massive catalyst and with increasing mean cluster size gradually approaches that on a massive catalyst, as can be seen from Fig. 19 for iridium.

Similar effects of increasing process rates on small clusters were also observed for other reactions: hydrogen ionisation, maleic acid electroreduction and formic acid electrooxidation (Fig. 20).

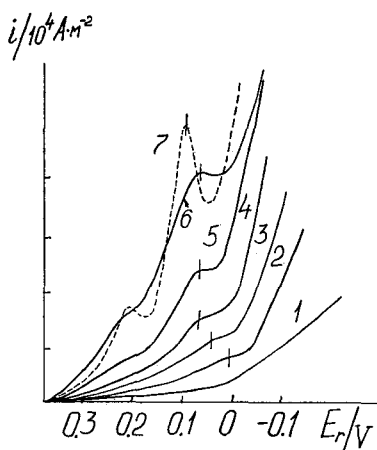


Fig. 19. The influence of size of cluster of iridium on titanium on the energy spectra of hydrogen adsorption. S_c/S_s : 1-0; 2-0.1; 3-0.25; 4-0.35; 5-0.52; 6-1.06; 7-Smooth iridium.

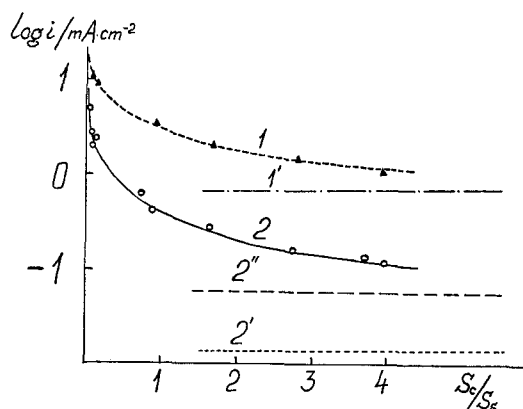


Fig. 20. Dependence of electroreduction rate of $5 \cdot 10^{-2}$ M maleic acid at $E_r = 0.05$ V (1) and electrooxidation rate of 1 M formic acid at $E_r = 0.3$ V (2) on the relative surface of microdeposits of iridium with respect to the titanium surface. 1', 2'-on smooth iridium; 1'', 2''-on smooth iridium and adatoms of titanium.

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The observed effects are due to a strong difference of the electronic and, as a consequence, adsorption properties of small size catalyst clusters from those of a massive electrode-catalyst. With increasing cluster size, these properties gradually approach those of the electron gas in massive metal.

The obtained results also showed that the effects for one and the same catalyst depend on the electrode-carrier nature. Thus the dependence of the electrocatalytic activity of microdeposits on their size is not general and is determined by the combination of the properties of catalyst and carrier.

To prove the determining role of electronic factors Skundin *et al* performed measurements on superfine continuous catalyst films on a carrier (<70 nm) and showed that the rate of hydrogen evolution is higher in this case and the adsorption energy lower than on a massive catalyst. Fig. 21 gives the dependence of the specific rate of hydrogen evolution on platinum films on glass carbon as a function of the film depositions time proportional to the film thickness.

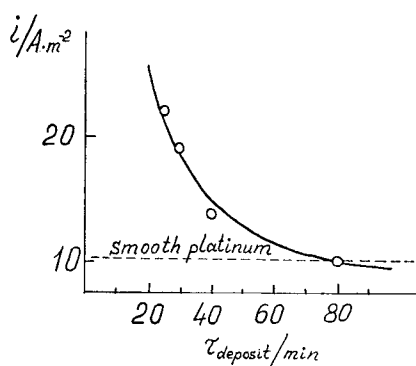


Fig. 21. Dependence of the specific rate of hydrogen evolution on platinum films on glass carbon on the film thickness (proportional to the film deposition time).

Photoemission measurements also point to a difference in the electronic properties of small clusters and a massive catalyst. As will be seen from Fig. 22 the photoemission current from platinum microdeposits on titanium in 1 M KOH in the presence of an acceptor- nitrous oxide is much greater than that from smooth platinum and platinized platinum. With increasing value of S_c/S_s , it gradually approaches the photocurrent on a platinized platinum electrode with the same roughness factor. It follows from the photoemission theory that the photoemission current is proportional to the density of electronic states of metal near the Fermi level. The data of the present study can be interpreted to mean that the density of electronic states in small clusters on a carrier increases. It is interesting to note that on palladium deposited on titanium no increase in photocurrents as well as in specific catalytic activity is observed. This clearly shows once more that the observed effects are defined by the combination of catalyst and carrier properties.

Promotion with Adatoms and microdeposits of catalysts

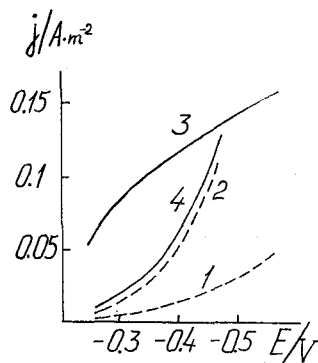


Fig. 22. Photoemission current from platinum microdeposits on titanium in 1 M KOH in presence of a acceptor (N_2O): 1-Pt/Pt, $S_c/S_s=4$, 3-Pt/Ti, $S_c/S_s=3.5$, 4-Pt/Ti, $S_c/S_s=100$, 2-Pt/Pt, $S_c/S_s=80$.

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